PB-213 410

TECHNICAL EVALUATION OF PHOSPHATE-FREE HOME LAUNDRY DETERGENTS

Helmut G. Reilich

IIT Research Institute
Chicago, Illinois

February 1972

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

W73-02351

PB 213 410

TECHNICAL EVALUATION OF PHOSPHATE-FREE HOME LAUNDRY DETERGENTS

by

Helmut G. Reilich
IIT Research Institute
Chicago, Illinois 60616

for the

Office of Research and Monitoring

ENVIRONMENTAL PROTECTION AGENCY

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Project No. 16080 DVF
Contract No. 14-12-937

-ia

February 1972

For sale by the Superintendent of Documents,
U. S. Government Printing Office, Washington,
D. C. - Price $1.25
SOD Order No. EP1.16:16080DVF 02/72

✓

SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

1. Report No.

2.

3. Accession No. **W**73-02351

4. Title TECHNICAL EVALUATION OF PHOSPHATE-FREE HOME LAUNDRY DETERGENTS,

5. Report Date

6.

8. Performing Organization Report No.

7. Author(s) Reilich, H[redacted] G.

10. Project No. EPA Program 16080 DVF 02/72

9. Organization IIT Research Institute, Chicago, Illinois

(CMC)

11. Contract/Grant No.

13. Type of Report and Period Covered

12. Sponsoring Organization

15. Supplementary Notes EPI·16:16080 DUF 02/72

Environmental Protection Agency, Water Pollution Control Research Series ~~[illegible]~~ February 1972. 120 p. 55 fig., 13 tab., 5 ref., 2 append.

16. Abstract

Phosphate-free detergents, using three surfactants which would be acceptable substitutes for conventional home laundry products, were formulated and evaluated. These surfactants are relatively safe, non-polluting, and biodegradable. The formulations are effective over a considerable water hardness range. Two of the surfactants investigated are about equally capable of yielding detergent formulations of high promise. All formulations contained 20% of the selected surfactant and 2% carboxymethylcellulose. The CMC, a well known soil suspending agent was used ad hoc on the basis of its well-established properties. Possible substitutes or optimum use level were not investigated. Although the point was not pursued as a specific end, indications are that use of these surfactants may lead to detergent formulations of lower basicity than currently in use, rendering them safer and less corrosive. They usually had a pH of about 10. A few at about pH 9 performed quite well. The formulation of choice had good overall detergent properties performing well under all test conditions and is essentially free of potentially polluting substances. Limited biological testing of these surfactants indicates safety relative to fish toxicity and lack of algal stimulating properties. (Jones-Wisconsin)

(a sulfonate or sulfonamide)

17a. Descriptors *Evaluation, *Laundering, *Detergents, *Formulation, Phosphates, Hardness (Water), Surfactants, Toxicity, Biodegradation, Hydrogen ion concentration, Economics, Sodium compounds, Electrolites, Water pollution control, Eutrophication, Testing, Chelation

17b. Identifiers *Phosphate-free detergents, Dishwashing detergents, Detergent builders

Copy available from GPO Sup Doc [redacted], $1.25; microfiche from NTIS as PB 213410, $0.95.

17c. COWRR Field & Group 05C

18. Availability ✓

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price -16-

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

128

R

Abstractor E. S. Jones va

Institution Wisconsin Univ., Madison

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Series describes the results and progress in the control and abatement of pollution in our Nation's waters. They provide a central source of information on the research, development, and demonstration activities in the water research program of the Environmental Protection Agency, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Inquiries pertaining to Water Pollution Control Research Reports should be directed to the Chief, Publications Branch (Water), Research Information Division, R&M, Environmental Protection Agency, Washington, D. C. 20460.

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Evaluation studies were carried out on a number of phosphate-free home laundry detergent formulations. These formulations were based on surfactants developed during the previous investigation sponsored by the Federal Water Quality Administration. These surfactants were selected because of the potential hard ion chelating properties and/or immunity to hard water effects. During the current program, they were also found to be non-toxic to marine life and to be biodegradable.

Separate series of formulations with each of three surfactants were evaluated. All formulations were aimed at the eventual development of a 100% solids, powdered product and contained 20% of the selected surfactant and 2% carboxymethylcellulose. The remainder of the formulations was varied using a number of known and safe conventional and unconventional components in various concentrations and combinations.

During the course of the project a combined total of 123 new formulations were evaluated. In addition, the original 15 formulations were reevaluated using a different type of cloth. The detergency effectiveness of these formulations was evaluated on two commercially produced, artificially soiled cotton test cloths. The effectiveness of 20 selected formulations was also evaluated on dacron/cotton wash-and-wear fabrics both with and without permapress finish. The detergency data compared favorably to that obtained with a standard phosphate containing detergent formulation supplied by the Association of Home Appliance Manufacturers (AHAM) and to a widely popular commercial brand.

This report was submitted in fulfillment of Project Number 16080 DVF, Contract No. 14-12-937, under the sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	3
III	Introduction	5
IV	Synthesis of the Surfactants	7
V	Biological Testing	11
VI	Evaluation of Detergent Formulations	13
VII	Acknowledgments	55
VIII	References	57
IX	Appendices	59

Preceding page blank

TABLES

No.		Page
1	Formulations for All Compounds	19
2	Formulations for Compound 112A	20
3	Formulations for Compound 112B1	22
4	Formulations for Compound 212	24
5	Formulation Components	27
6	Normalization of UST Cloth Data	34
7	Detailed Performance Ranking of 112A Formulations - UST Cloth	38
8	Detailed Performance Ranking of 112A Formulations - EMPA Cloth	40
9	Detailed Performance Ranking of 112A Formulations - Combined Cloths	42
10	Summary of Performance Ranking of Compound 112B1 Formulations	44
11	Summary of Performance Ranking of Compound 212 Formulations	46
12	Whiteness Retention - 112A Formulations	52
13	Whiteness Retention - 212 Formulations	53

Preceding page blank

FIGURES

No.		Page
1	Regular vs Combined Washing AHAM in 50 ppm Hardness Water	16
2	Regular vs Combined Washing AHAM in 135 ppm Hardness Water	17
3	Regular vs Combined Washing AHAM in 300 ppm Hardness Water	18
4	Comparison of Two Batches of EMPA Cloth	29
5	AHAM on UST Cloth 50 ppm Hardness Water	30
6	AHAM on UST Cloth 135 ppm Hardness Water	31
7	AHAM on UST Cloth 300 ppm Hardness Water	32

Preceding page blank

SECTION I

CONCLUSIONS

The results obtained during the course of this project indicate that effective phosphate-free home laundry detergents can be formulated using specific anionic surfactants and builders which are relatively safe and non-polluting. The results also show that these formulations can be effective over a considerable range of water hardness. Indications also are that several nearly equally effective formulations can be developed.

Two of the three surfactants investigated, sodium dodecylbenzenesulfonamidoethyl sulfate ($C_{12}H_{25}$-C_6H_4-$SO_2NHCH_2CH_2$-OSO_3Na, 112A) and methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)propionate ($C_{12}H_{25}$-C_6H_4-$COCH(SO_3Na)CH_2CO_2CH_3$, 212), are about equally capable of yielding detergent formulations which show high promise of being acceptable substitutes for the current high-phosphate products. The third surfactant, sodium dodecylbenzenesulfonamidoethyl sulfone ($C_{12}H_{25}$-C_6H_4-$SO_2NHCH_2SO_3Na$, 112B1), although promising, yielded no formulation during the current project which were competitive with those obtained for the former two compounds.

All formulations evaluated contained 20% of the selected surfactant and 2% carboxymethylcellulose (CMC). The CMC, a well known soil suspending agent, was used ad hoc on the basis of its well-established properties, and no attempt was made to investigate possible substitutes or to determine the optimum use level. Although the point was not pursued as a specific end, indications are that the use of these surfactants may lead to detergent formulations of lower basicity than those currently in use rendering them safer and less corrosive. Most of the formulations tested had a pH of about 10 but a few which were tested at about pH 9 performed quite well.

Of the several potential builders investigated sodium acetate, sodium citrate and sodium gluconate had the greatest beneficial effect, especially when used in combination with each other. Electrolites, such as sodium chloride and sodium sulfate, also contributed to the effectiveness of some of the formulations. Sodium carbonate, on the other hand, had only a relatively minor effect in improving the performance of these surfactants.

SECTION II

RECOMMENDATIONS

The ability of the surfactants under consideration to produce phosphate-free detergent formulations has now been demonstrated on the basis of laboratory evaluation. A further evaluation of a number of other factors is now indicated. These factors include (1) thorough biological and safety testing, (2) consumer acceptability, (3) potential effect of large scale use on the environment, (4) further optimization of product efficiency, (5) feasibility of using these surfactants in developing phosphate-free dishwasher detergents, and (6) economic considerations.

Although preliminary investigation shows that the surfactants 112A and 212 are safe, full-scale biological and safety testing should be undertaken. Since these surfactants have not been used for this purpose before and their behavior is not well established, such testing is imperative. Fully built candidate formulations should be included in these tests to insure that no untoward synergistic effects are manifested.

Consumer acceptability testing and the potential effect of large scale use of these detergents should be assessed. These two studies can be carried out simultaneously by placing a selected formulation in a relatively isolated community which has its own sewage treatment plant. A large scale production of one or more formulations should be undertaken and the product offered for use by all the households in the selected community for a period of several months. A good estimate of consumer acceptance could be derived from opinions of the people using the product. Monitoring the effluent waters from this community both before and after treatment would provide insight both into the effect of the removal of phosphate from laundry detergents as well as the specific impact on the ecology of using the candidate surfactant. Such a study would be doubly useful since it would also provide data relative to the need to possibly consider the removal of other sources of phosphate, e.g., automatic dishwasher detergents, in order to effectively counteract eutrophication.

The formulation which we are recommending for the broad range study is 112A-121. This formulation is not the only effective formulation developed during this program nor do we intend to imply that it is necessarily the best possible formulation which can be developed using these anionic surfactants. This is particularly true since one of the most promising formulation components, nitrilotriacetate (NTA), was not evaluated because its use in detergents was

Preceding page blank

in serious doubt during most of the time during which this program was in effect. Further efforts towards the optimization of effectiveness of formulations based on these surfactants is therefore indicated. This effort should be extended to both compounds 112A and 212. Data indicates that the latter can yield detergent formulations at least as efficient as the former.

Considering that the number of automatic dishwashers in use in our society is rapidly increasing and that most detergents designed for use in these machines contains an exceedingly high amount of phosphates, up to 90%, some thought should now also be given the potential thread of phosphate pollution from this source. It is therefore recommended that a similar study to determine the feasibility of using these or analogous surfactants for formulating phosphate-free dishwasher detergents be undertaken.

Since these surfactants are not now in commercial production, a study to estimate their potential cost should be undertaken. The economic impact on the market of builders used in the proposed formulations is also merited. Such cost data would be useful in promoting, by the government, the production of these phosphate-free home laundry formulations to industry.

SECTION III

INTRODUCTION

Eutrophication of the Nation's lakes and rivers has become a major problem causing great concern to government, industry and the public. Phosphates in particular have been singled out as being to a large extent responsible for this eutrophication. Detergents, of which phosphates are a major component, are among the main sources of the phosphates which reach our waterways. Much pressure has therefore been exerted to urge government and industry to find detergent formulations which are free of phosphates and other polluting substances. While it has been suggested that an alternate solution, namely, the building of vast tertiary sewage treatment plants, capable of removing the phosphates from the sewage be initiated, the elimination of the sources of pollution still remains the most logical approach.

During a previous project[1] we demonstrated the feasibility of formulating home laundry detergents using a novel series of surfactants which have the ability to avoid the interference from the hard water ions to which the conventional surfactants and soaps are susceptible. This immunity to hard water effects eliminates the need for strong chelating agents which is one of the major functions of phosphates. The other functions usually attributed to the phosphates, solids suspension by deflocculation and reserve alkalinity could then be provided by the judicious selection of other components used to make up the fully built home laundry detergent formulation.

Work on the previous project indicated that three of the several surfactants investigated had definite promise for the successful formulations of phosphate-free laundry detergents. These compounds were sodium dodecylbenzenesulfonamidoethyl sulfate (112A), sodium dodecylbenzenesulfonamidoethyl sulfonate (112B1) and methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)propionate (212).

This project then, consisted of formulation and evaluation of phosphate-free detergents, using the above surfactants, which would be acceptable substitutes for conventional home laundry products.

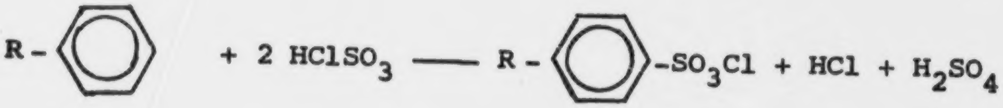
SECTION IV

SYNTHESIS OF THE SURFACTANTS

The synthesis of the candidate surfactants was discussed in detail in the previous report.[1] Efforts during the second year of this project were aimed primarily at upgrading the yields and at defining the parameters for scaling up the reactions to eventual pilot plant size production of the selected compound. The synthesis of the three surface active agents selected for further development is reviewed in the following paragraphs which include also some pertinent experiments to defining the parameters for the optimization of the reactions.

Synthesis of Surfactants 112A and 112B1

It had become apparent that on the basis of NMR spectra these two surfactants, as used in the earlier evaluations, were only about 60% pure, the remainder of the titratable surfactant being LAS. The reaction conditions for the sulfonation of the alkylbenzene were studied critically. It appeared that the reaction took place readily at room temperature either in the absence or presence of chlorinated hydrocarbon. Primarily, for reasons of ease of handling it was found useful to add a fair amount of dichloroethane which markedly reduces the viscosity of the product. Using this approach, it was observed that the reaction mixture after standing for at least 4 hrs at room temperature or overnight settles out a very dark lower layer of spent sulfuric acid. The density of this lower layer is approximately 1.8 which is close to that of sulfuric acid. In this manner, we were able to remove about 70-75% of the sulfuric acid formed during the course of the following reactions:



Running the sulfonation at a higher temperature did not affect the yield but caused a marked darkening of the organic layer which made the separation of layers much more difficult.

It had been assumed that the sulfonyl chloride formed in the above reaction would decompose quite readily in water

Preceding page blank

or alkali which, however, turned out not to be the case. The sulfonyl chloride when stirred with aqueous sodium hydroxide at 80°C did not decompose to any significant extent. Upon addition of DMSO hydrolysis did occur, requiring about 1/2 hr at 80°C. The relative stability of the sulfonyl chloride and the use of a mutual solvent appeared to be a key to improving the yield of the product.

None of the spectra of the product show any significant amount of hydrocarbon so that it can be assumed that the sulfonation with chlorosulfonic acid is a reasonably quantitative one. The conversion to the sulfonyl chloride is not entirely quantitative. By dispersing the sulfonyl chloride in water and neutralizing this suspension with sodium hydroxide, we would presumably convert all unreacted sulfonic acid to LAS. On the basis of a cationic titration, the crude sulfonyl chloride proved to contain about 6% unreacted sulfonic acid.

In order to expedite the conversion to the sulfonamide surfactants 112A and 112B1, we found the use of DMSO to be of some advantage. One disadvantage of using DMSO was later found in the scaled up experiments where it was extremely difficult to completely remove this solvent from the product. The reaction proceeds best if carried out at room temperature. The synthetic procedures for the two surfactants are entirely analogous as outlined in the following sections.

Synthetic Procedure

47.2 g of dodecylbenzene (Continental Oil Nalkylene 500) were dissolved in 50 ml of dichloroethane. 51.3 g of chlorosulfonic acid were added slowly at room temperature while cooling with a water bath. The mass was then transferred to a separatory funnel and allowed to settle for 4 hrs. The mass became cloudy after about 2 hrs and a darker layer of black sulfuric acid settled on the bottom. After 4 hrs this bottom layer of 16 g was discarded. 27 g of sodium hydroxide were dissolved in 125 ml of water and the solution cooled to room temperature. 15 ml of DMSO were then added followed by 28 g of aminoethyl hydrogen sulfate. After all or most of the latter had dissolved at room temperature, the sulfonyl chloride solution was added slowly to this solution with good cooling with an ice or water bath in order to maintain the temperature at or below 25°C. Stirring was continued without further cooling. After about 2 hrs, the initially milky white reaction mass turned somewhat more translucent and yellowish and the viscosity of the mass increased substantially. The pH dropped rapidly to 8. Occasionally, a pH drop to 5 occurred in which case a few pellets of solid sodium hydroxide were added to bring the pH back to 8-9. Stirring at room temperature was continued until no further pH drop was observed for at least 30 min. Then 10 ml of dichloroethane and 30 ml of isopropanol were added whereupon the viscosity dropped substantially. The reaction mass was then heated to 60°C and placed in a separatory funnel. A lower aqueous layer amounting to 75-80 ml was drawn off and discarded. The top layer was placed in a rotary evaporator to remove the chlorinated solvent. A small part of the resulting geletanous mass was dried further for NMR analysis. The remainder was usually dissolved in a mixture of 30% isopropanol in water since it was easier to use in this form for most of our test formulations. A conversion of about 80±5% was obtained by this procedure.

Surfactant 112B1 was synthesized in exactly the same manner as above except that 25 g of taurine were used in place of the aminoethyl hydrogen sulfate. In this case, the conversion also amounted to 85±5%.

No difficulties were encountered in scaling up the synthesis of these two surfactants. Batches using more than ten times (3 moles) the above quantities were successfully made in the laboratory. It is not expected that pilot plant and larger production of these compounds should present any significant problems provided that proper corrosion resistant equipment is used.

Synthesis of Sulfopropionate Surfactant 212

The acrylic acid intermediate was prepared as follows: 49 g (0.5 M) of maleic anhydride was mixed with 110 g of dry dichloroethane in a 3-neck flask equipped with a thermometer, magnetic stirrer, dropping funnel and a reflux condenser which was topped with a drying tube. The anhydrous aluminum chloride (120 g, 0.9 M) was added with cooling and, after ten minutes of stirring, 118 g (0.5 M) of dried dodecylbenzene (Continental Oil Company, Nalkylene 500. MW 236) was added slowly while maintaining the temperature at 20°C. After stirring at room temperature for one hour, the viscous dark brown mixture was poured into a beaker containing 450 g of ice, 50 ml of 66% sulfuric acid and 15 ml of isopropyl alcohol. After thorough mixing, the bright yellow mixture was allowed to stand and the upper layer was separated and washed twice with 70 ml portions of 66% sulfuric acid which contained 10 ml of isopropyl alcohol. The unsaturated keto acid solution in dichloroethane was heated to 70°C to remove a water layer. For the purpose of infrared and PMR spectra, the organic layer was stripped of solvent under reduced pressure, leaving a viscous amber liquid. Basic titration of this material required 2.75 meq/g. The theoretical value for the acrylic acid intermediate is 2.91 meq/g.

The solution was then esterified with 19.2 g of methanol (0.6 M) and 5 ml of concentrated sulfuric acid (or 2 g of toluenesulfonic acid). The solution was heated at reflux for 3/4 of an hour, the lower aqueous layer was separated and discarded and an additional 12.8 g (0.4 M) of methanol and 2 ml of concentrated sulfuric acid (or toluenesulfonic acid) were added. After refluxing for an additional 1 1/2 hours the organic layer was separated and the solvent was removed under reduced pressure. Titration of the residual oil with standardized ethanolic potassium hydroxide solution showed the acid content to be less than 4%.

Conversion of the acrylate to the desired surfactant, 212, was accomplished by the addition of sodium bisulfite across the double bond. A Parr pressure reactor was charged with the ester and 52 g (0.5 M) of sodium bisulfite in 140 ml of water. The mixture was heated in the sealed container with stirring for 3 hours at 110-120°C. The yellow mixture was removed and dried in a vacuum oven at 55°C/13 torr. The anion content of this material was typically 2.01 meq/g as determined by cationic titration. The theoretical value for the surfactant is 2.23 meq/g, inferring ca. 90% purity.

SECTION V

BIOLOGICAL TESTING

While the full range of biological testing of our surfactants was not within the scope of the current program, preliminary fish toxicity tests and algae stimulation tests were carried out. During the previous year's program the biodegradability of these compounds had already been established to be of the same order as that of the linear alkylbenzenesulfonates widely used in today's phosphate containing detergents. The tolerance limit median (TLm) study using fingerling fathead minnows and the "provisional algae assay procedures" (PAAP) on the three candidate surfactants and a control sample of LAS were performed under subcontract by Biometric Testing Inc., Englewood Cliffs, New Jersey. Their report, describing in detail all the methods used, is appended hereto.

The 96 hr TLm values, as reported by Biometrics, were somewhat lower for the three candidate surfactants than for the two aliquots of the same lot of LAS. The 96 hr dynamic phase TLm values were 2.0 ppm for surfactant 112A, 6.0 ppm for 112B1, and 3.2 ppm for 212 as compared to values of 12.0 ppm and 9.5 ppm for the two samples of LAS. Dissolved oxygen values for all compounds during these tests ranged from 7.0 ppm to 10.5 ppm.

The results of the PAAP test using the alga *Selenastrum capricornutum* compared favorably with those obtained with LAS. The increases in the number of algae cells between the 5th and 7th day for LAS over the increase in the cell count for the corresponding control were by factors of 1.13, 1.41 and 1.37, respectively, for concentrations of 5.0 ppm, 0.5 ppm and 0.05 ppm LAS. These increases were by factors of 1.16, 1.33 and 1.20 for concentrations of 3.0 ppm, 0.3 ppm and 0.03 ppm of surfactant 112B1; and 1.11, 1.55 and 2.16 for concentrations of 1.8 ppm, 0.18 ppm and 0.018 ppm, respectively, of surfactant 212. Surfactant 112A showed a slight apparent inhibition effect where cell counts between the 5th day and the 7th increased to a somewhat lesser degree than those for the corresponding control. At concentrations of 1.4 ppm, 0.14 ppm and 0.014 ppm, compound 112A gave factors of 0.47, 0.77 and 0.68, respectively.

SECTION VI

EVALUATION OF DETERGENT FORMULATIONS

Test Procedures

The advantages to using a laboratory bench-scale device capable of simulating the action of a washing machine over the use of an actual full-scale commercial machine are manyfold, especially where rapid evaluation of a large number of formulations is required. The expense and time consuming gathering and processing of large numbers of full-sized laundry bundles is avoided and a test can be run in about 20 min instead of 1-2 hrs. Further savings in cost and time result from the fact that only relatively small quantities of the test formulations need be made up and the use of a full scale washing machine almost precludes the testing at water hardnesses other than that normally available locally. Finally, where correlation of a large number of comparative data is required for critical evaluation of formulation components, the bench-scale equipment permits the necessary control of the conditions to be used.

All of the evaluations on this project were therefore carried out using a bench-scale simulated washing machine. The machine used was a "Tergotometer" Model 7243 manufactured by U. S. Testing Co. of Hoboken, New Jersey. This instrument permitted the close control of the wash water temperature, detergent concentration, speed and timing of the wash and rinse cycles. In addition, this model has four separate washing stations so that it was possible to run four samples or concentrations simultaneously. The conditions used for all tests were a machine speed of 150 rpm and wash water temperature of 120°F. The wash cycle was 15 minutes and the rinse cycle 2 minutes. The tests were run at three water hardness levels of 50, 135 and 300 ppm. The 135 ppm level represents the nominal hardness of Chicago tap water which was used directly. The 50 and 300 ppm waters were made up by adding to appropriate amounts of calcium and magnesium chlorides to distilled water or to tap water, respectively.

The soil as well as the cloth used for testing the effectiveness of detergents is of critical importance. A great number of investigations have been reported in the literature on the significance of these two parameters and a number of soil compositions ranging from iron compounds,[2] Clay,[3] clay-oleic acid combinations[4] to vacuumed carpet soil[5] have been developed and proposed as being more or

Preceding page blank

less representative of the soil found in normal laundry bundles. Several companies, both in the U. S. and abroad, provide pre-soiled test cloths on a commercial basis. The soils used for these cloths vary with the manufacturer and the purpose for which the cloths are intended. Basically, these soils are compositions of several commonly found materials including vegetable and/or mineral oil, starches, proteinaceous derivatives and other organic and mineral components. Carbon (lamp black) is added to these soils to provide a constant coloring which may be used for the optical evaluation. The soil is transferred onto the cloth by either cloth dyeing or printing methods capable of providing a reasonably consistent product. Here again, the choice of using commercially available soiled cloth over soiled cloth made in our own laboratories was dictated by two main considerations. The availability of large quantities of soiled cloth of sufficient consistency to yield readily correlatable detergency data gathered over a protracted period of time was essential. Producing such quantities of cloth on a laboratory scale is extremely cumbersome and requires an inordinate expenditure of time if strict quality control is to be exercised.

The soiled cotton cloth supplied by U. S. Testing Co. (UST) which had been used during the previous year's work was again utilized during this project. In addition, a second soiled cotton cloth, EMPA-101, was used for all of the test formulations produced during the present program and many of the previous formulations were retested on this cloth. This cloth is produced in Switzerland for the Eidgenossischematerialprufunganstalt (EMPA) and supplied in the U. S. by Testfabrics, Inc. Selected formulations were further tested on two types of dacron/cotton (65/35) shirting made by Testfabrics, Inc., New York, New York. One of these fabrics had a permapress finish while the other was without finish.

During the earlier work using only a single type of test cloth three 4 1/2 x 5" swatches were placed in the Tergotometer container and washed in 750 ml of detergent solution. After the addition of a second type of cloth to our testing program, the method was changed to enable us to run both cloths simultaneously thus allowing us to evaluate the same number of formulations in a given time as with the single cloth method. This procedure had been investigated in connection with another project and proved suitable for use here. This method combines the washing of both the UST and the EMPA cloths in a single run. Three swatches of each are placed in the same Tergotometer container and washed together instead of making a separate washing for each type of cloth. The size of the swatches was reduced to 4 x 4" and in order to partially compensate for the increased amount of material to be washed, the amount of detergent solution used was increased from 750 ml to 1000 ml. Although the overall results obtained by this method are generally lower than those obtained when the cloths are washed separately, the resulting curves are, for all practical purposes, parallel and differences between the effectiveness of the various formulations are similar. The results for AHAM are illustrated in Figures 1-3.

In order to be able to monitor the test procedures and to permit normalization of data where two different lots of cloth yielded significantly different detergency results, two commercially formulated detergents were used for reference purposes. One was a standard detergent formulation provided by the American Home Appliance Manufacturers Association under the label AHAM-2A. The other was a popular home laundry product purchased at the local super market. This widely used high phosphate brand also provided us with performance data which we felt we should attempt to match in order to insure potential consumer acceptance of our non-phosphate formulations.

Formulation

Since the prime objective of the present program was to develop one or more phosphate-free detergent formulations which could readily be substituted for the high phosphate products now in use, it was desirable to aim for a solid, powdered formula of the general type of those common today and in the use of which the housewife is familiar with. An extended, built formulation was preferable since, in the opinion of many experts, detergent concentrates have, in the past, always encountered an undue degree of consumer resistance. Finally, a powdered detergent, due to the design of most existing washing machines, is more easily and safely handled than a liquid formulation.

For these reasons, all of our experimental formulations were formulated with a view toward eventually building a 100% solids product. The percentage values given for the various components in Tables 1 to 4 and in the following discussion are on the basis of partially built formulations with the balance in each case being water. Thus, all formulations contained 20% surfactant, 2% carboxymethylcellulose (CMC), the given percentages of other components plus, in most cases, water. The actual percent total solids is given in the line below the ingredients of the

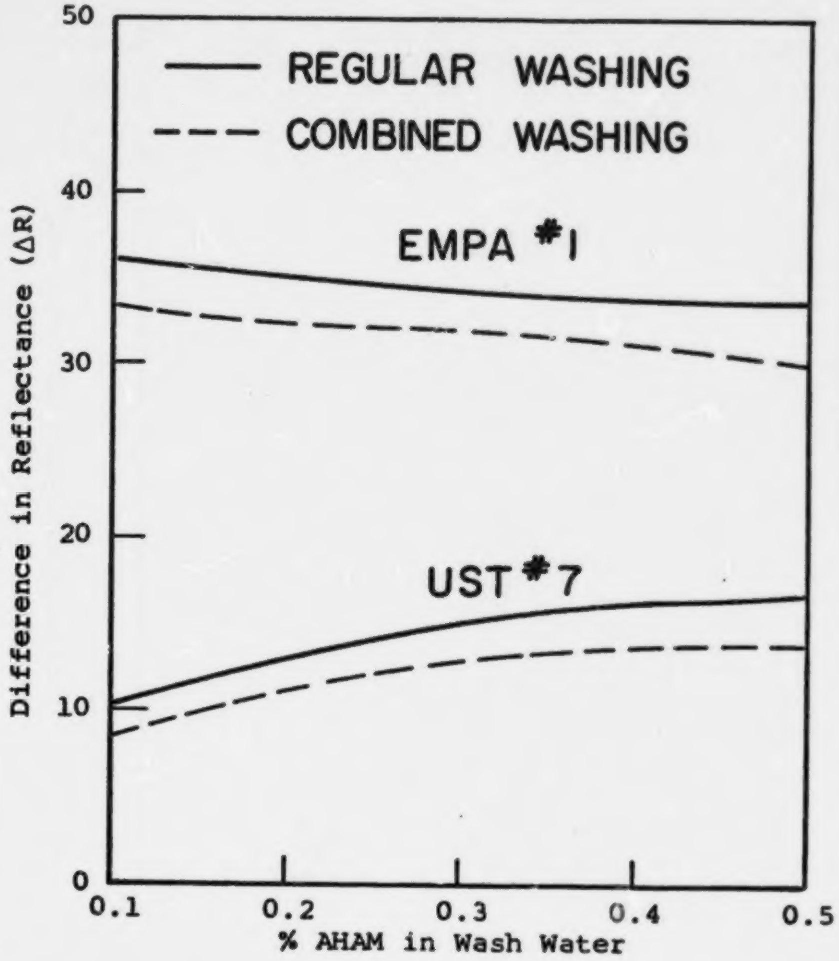


Figure 1

REGULAR VS COMBINED WASHING
AHAM in 50 ppm Hardness Water

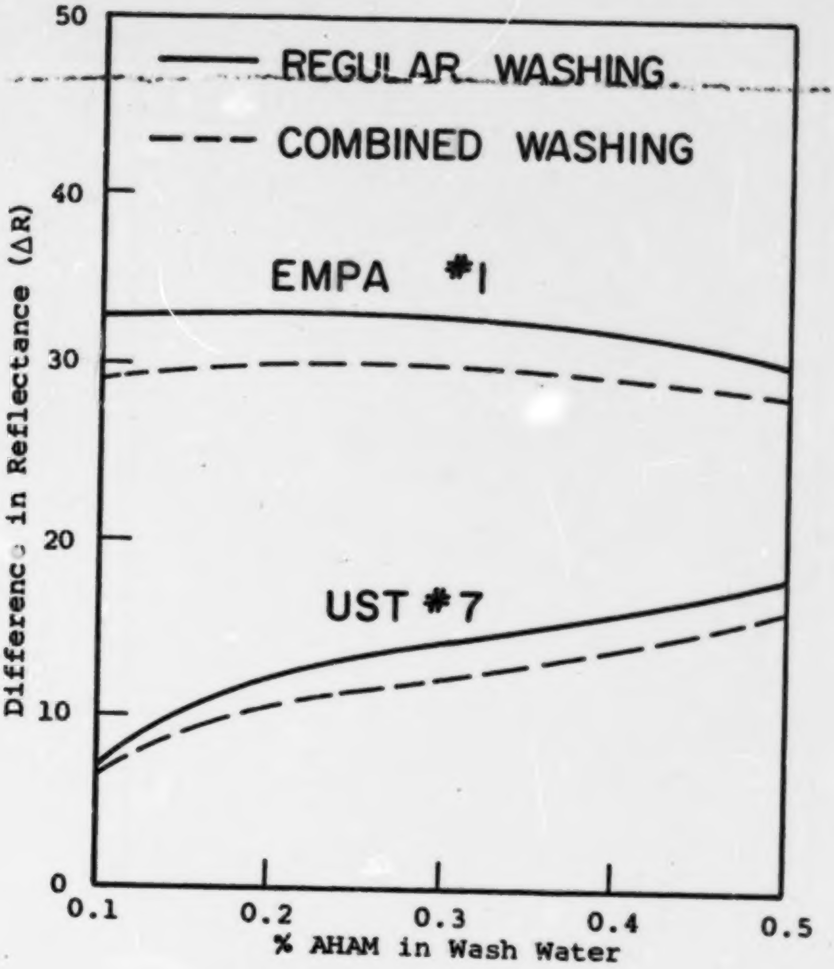


Figure 2

REGULAR VS COMBINED WASHING
AHAM in 135 ppm Hardness Water

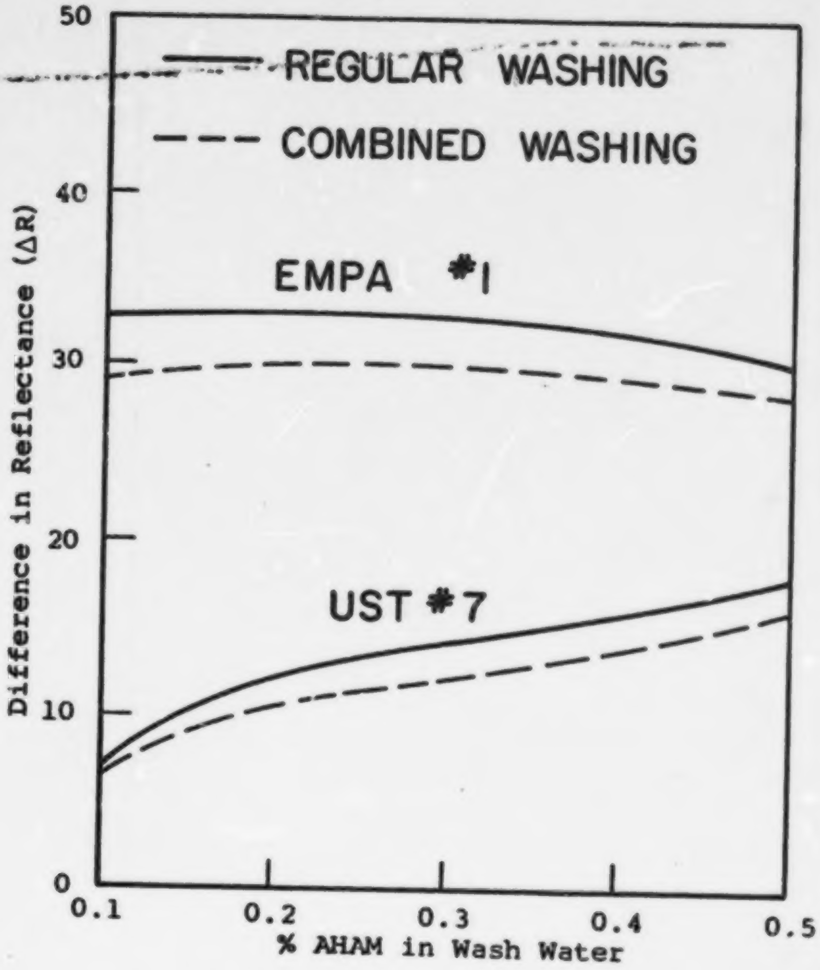


Figure 2

REGULAR VS COMBINED WASHING
AHAM in 135 ppm Hardness Water

Table 1

FORMULATIONS FOR ALL COMPOUNDS[a]

Components	G	A	E	L	C	CC	H	I	II	F	D	J	K	B	N	M	O	Brand	AHAM
Silicate[b]	14.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	2.8	10.1	10.1	10.1	8.4	8.4	8.4		
Carboxymethylcellulose	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
Cocodiethanolamide	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
Sodium Acetate	-	-	30	-	-	-	-	-	-	-	30	30	22	22	20	20	20		
Sodium Citrate	-	-	-	17	-	-	-	-	-	-	-	-	-	-	-	-	-		
Sodium Carbonate	-	-	-	-	40	10	-	-	-	-	-	-	-	-	-	10	-		
Sodium Chloride	-	-	-	-	-	-	10	-	-	-	-	-	-	-	-	-	-		
Sodium Sulfate	-	-	-	-	-	-	-	10	40	-	-	-	-	15	-	-	10		
Trisodium Nitrilotri-acetate (NTA)	-	-	-	-	-	-	-	-	-	17	-	17	17	-	-	-	17		
Tergitol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Seqlene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Sodium Gluconate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Gantrez-AN 119	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Weston	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Total Solids[c]	38	34	64	51	74	44	44	44	74	51	57	81	73	71	52	62	79		
Ranking for 112A Formulations[d]																			
UST Cloth (63)	41	29	47	18	28	30	52	49	38	33	45	50.5	43	48	39	55	59	61	44
EMPA Cloth (59)	6	1	4	7	19	40	2	14	11	-	8	58	-	-	55	5	47	59	49
Combined Cloths (59)	11	1	14.5	3	24	38	21	29	15	-	20	58	-	-	57	28	56	59	54.
Ranking for 112B Formulations[d]																			
UST Cloth (57)	48	27	50.5	11	44	13	56	34	22	32	50.5	52	41	40	39	47	49	57	45
EMPA Cloth (56)	1	4	25	12	14	9	5	3	10	52	2	8.5	33.5	-	18	16	39	56	41
Combined Cloths (56)	1	7	34	13	19	4	10	5.5	9	55	2	35	36	-	23	27.5	47	56	45
Ranking for 212 Formulations[d]																			
UST Cloth (53)	32	35	45	5	24	31	48	41	40	27.5	34	27.5	26	46.5	29	50.5	37	53	46.5
EMPA Cloth (47)	3	1	16	34	11	12	6	2	25	33	13	-	-	-	8	17	36	47	45
Combined Cloths (47)	2	1	18	19	11	12	13	3	27	30	17	-	-	-	9	25	45	47	46

---

[a] All formulations contain 20% surfactant.

[b] "Star" silicate, except as otherwise noted.

[c] Total solids include 20% surfactant; balance = water.

[d] Weighted rank values; figures in parentheses indicate total number of samples ranked in set: 1 = worst, highest value = best.

Table 2

FORMULATIONS FOR COMPOUND 112A[a]

Components		7	25	26	32	33	34	35	49	50	51	52	58	59	60	61	62	72	73	75	76	77	78
Silicate[b]		10.1	10.1	10.1	10.1	5.0	10.1	10.1	0	9.8	10.1	10.1	N 10.1	N 5.0	N 10.1	0	0	N 10.1	10.1	N 5.0	N 5.0	0	0
Carboxymethylcellulose		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.9	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Cocodiethanolamide		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.9	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0	0	2.0	2.0	2.0	2.0
Sodium Acetate		-	20	20	20	20	20	20	20	19.2	-	-	20	20	20	20	20	-	-	20	20	20	20
Sodium Citrate		-	-	-	17	17	17	17	17	28.3	-	-	17	17	17	17	17	-	-	30	30	30	30
Sodium Carbonate		-	-	10	-	-	10	-	10	-	-	-	-	-	-	-	-	-	-	10	-	-	10
Sodium Chloride		10	10	10	-	-	-	10	-	9.6	-	10	-	-	10	-	-	-	-	-	-	-	-
Sodium Sulfate		10	10	-	-	-	-	-	-	9.6	-	-	-	-	-	-	-	-	-	-	-	-	-
Trisodium Nitrilotri-acetate (NTA)		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tergitol		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5	-	-	-	-
Seqlene		-	-	-	-	-	-	-	-	-	10	10	-	-	-	-	-	-	-	-	-	-	-
Sodium Gluconate		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gantrez-AN 119		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Weston		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
																pH10→	pH7[e]						
Total Solids[c]		54	74	74	71	66	81	81	71	100	44	54	71	66	81	61	61	32	37	89	79	74	84
Rank:[d]	UST Cloth (63)	13	19	42	14	24	25	37	46	20	36	27	31.5	31.5	16	22	2	58	35	11	6	9	1
	EMPA Cloth (59)	17	-	38	37	45	46	35	12	33	20	13	26	22	29	24	16	51	3	56	43	57	41
	Combined Cloth (59)	7	-	46	22	43	45	37	25	33	27	10	32	26	13	17	2	55	6	49	23	52	16

Table 2 (cont.)

Components	79	80	81	103	104	105	111	112	113	114	115	116	118	119	120	121	122	123	124	125	126	127		
Silicate[b]	10.1	10.1	10.1	N 5.0	N 5.0	N 5.0	N 5.0	10.1	10.1	10.1	10.1	10.1	N 5.0	0	0	10.1	10.1	N 10.1	N 10.1	N 10.1	N 5.0	N 5.0		
Carboxymethylcellulose	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
Cocodiethanolamide	2.0	2.0	2.0	2.0	2.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
Sodium Acetate	-	20	-	20	20	20	20	20	20	-	20	-	20	20	20	20	20	20	20	20	20	20		
Sodium Citrate	-	-	17	20	20	30	30	-	-	-	-	-	30	30	30	20	-	-	-	-	20	20		
Sodium Carbonate	-	-	-	-	10	10	-	-	10	-	-	-	-	-	-	-	10	-	-	-	-	-		
Sodium Chloride	-	-	-	-	10	-	-	-	-	-	-	10	10	10	10	10	10	10	10	10	10	-		
Sodium Sulfate	-	-	-	10	10	-	-	-	-	-	-	10	-	-	-	-	-	10	10	10	10	-		
Trisodium Nitrilotriacetate (NTA)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Tergitol	-	-	-	-	-	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Seqlene	-	-	-	-	-	-	-	-	-	-	10	-	-	-	-	-	-	-	-	-	-	-		
Sodium Gluconate	10	10	10	-	-	-	10	20	10	-	-	-	10	10	10	17	20	20	20	20	-	-		
Gantrez-AN 119	-	-	-	-	-	-	-	-	-	1.0	-	-	-	-	1.0	1.0	-	-	1.0	5.0	-	-		
Weston	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	10		
Total Solids[c]	44	64	61	74	99	92	87	72	72	33	62	52	97	92	93	100	92	92	93	97	97	77	Brand	AHAM
Rank:[d] UST	56	57	5	12	17	7	15	63	50.5	60	55	62	23	10	3	26	34	54	40	21	8	4	61	44
EMPA	10	30	34	21	50	36	52	18	48	23	9	28	53	27	25	54	42	15	32	31	39	44	59	49
Combined	34	50	14.5	5	42	8.5	36	39	53	41	12	47	48	8.5	4	51	44	33	39.5	30	18	31	59	54

---

[a] All formulations contain 20% surfactant.

[b] "Star" silicate, except as otherwise noted.

[c] Total solids include 20% surfactant; balance = water.

[d] Weighted rank values; Figures in parentheses indicate total number of samples ranked in set: 1 = worst, highest value = best.

[e] Titrated to pH7 with citric acid.

Table 3

FORMULATIONS FOR COMPOUND 11281[a]

Components	20	21	22	36	37	38	39	40	41	63	64	65	66	67	70	71	82	83
Silicate[b]	10.1	10.1	9.8	10.1	10.1	10.1	10.1	10.1	10.1	N 10.1	N 10.1	N 10.1	0	0	10.1	10.1	N 10.1	N 10.1
Carboxymethylcellulose	2.0	2.0	1.8	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Cocodiethanolamide	2.0	2.0	1.8	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0	0	0	0
Sodium Acetate	-	-	-	-	20	20	-	20	20	20	20	-	20	20	-	-	20	20
Sodium Citrate	-	-	-	-	-	20	20	20	20	20	20	20	20	20	-	-	20	-
Sodium Carbonate	-	40	36	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sodium Chloride	-	-	-	10	10	-	10	10	10	-	10	10	-	-	-	-	-	10
Sodium Sulfate	20	20	18	10	10	-	-	-	10	-	-	-	-	-	-	-	-	-
Trisodium Nitrilotriacetate (NTA)	-	-	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tergitol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5	5	5
Seqlene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sodium Gluconate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gantrez-AN 119	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Weston	-	-	-	-	-	-	-	-	-	-	-	-	- pH9+	- pH7[e]	-	-	-	-
Total Solids[c]	54	94	100	54	74	74	64	84	94	74	84	64	64	64	32	37	77	67
Rank:[d] UST Cloth (53)	7.5	3	21	39	36	20	22	9	12	19	23	33	6	16	38	17	4	2
EMPA Cloth (47)	-	-	-	27	28	42	43	31	22	30	37	26	14	15	24	9	46	39
Combined Cloth (47)	-	-	-	33	32	41	43	22	15	29	36	31	7	10	26	6	44	30

Table 3 (cont.)

Components	84	85	86	87	88	97	98	99	100	101	102	106	107	108	109	110		
Silicate[b]	10.1	10.1	10.1	10.1	2.5	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1		
Carboxymethylcellulose	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
Cocodiethanolamide	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0	0	0	0	0		
Sodium Acetate	-	-	-	-	30	20	20	20	-	-	-	20	20	20	-	20		
Sodium Citrate	-	-	-	-	-	20	20	20	20	30	30	-	20	20	-	-		
Sodium Carbonate	-	-	-	-	20	-	-	-	-	-	-	-	-	-	-	-		
Sodium Chloride	-	10	-	10	-	-	-	10	-	-	10	-	-	-	-	-		
Sodium Sulfate	-	-	-	-	-	25	20	15	25	25	25	-	-	10	-	-		
Trisodium Nitrilotriacetate (NTA)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Tergitol	-	-	-	-	-	-	5	-	-	-	-	-	-	-	-	-		
Seqlene	10	10	-	-	-	-	-	-	-	-	-	10	10	10	-	-		
Sodium Gluconate	-	-	10	10	-	-	-	-	-	-	-	-	-	-	-	-		
Gantrez-AN 119	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	1		
Weston	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Total Solids[c]	44	54	44	54	76	99	99	99	79	89	99	62	82	92	33	53	Brand	AHAM
Rank:[d] UST	43	42	44	30	25	13	1	18	14	10	11	50.5	7.5	15	49	52	53	46.5
EMPA	18	7	4	5	29	23	10	35	38	41	44	20	32	40	21	19	47	45
Combined	21	14	8	5	23	16	4	24	28	34	38	37	20	40	35	42	47	46

[a] All formulations contain 20% surfactant.

[b] "Star" silicate, except as otherwise noted.

[c] Total solids include 20% surfactant; balance = water.

[d] Weighted rank values; Figures in parentheses indicate total number of samples ranked in set: 1 = worst, highest value = best.

[e] Titrated to pH7 with citric acid.

Table 4

FORMULATIONS FOR COMPOUND 212[a]

Components	28	29	30	31	42	43	44	45	46	47	48	53	54	55	56	57	68	69	74	89	90
Silicate[b]	10.1	10.1	10.1	10.1	9.7	8.8	20.2	20.2	20.2	20.2	20.2	N 10.1	N 10.1	N 10.1	0	0	10.1	10.1	4.2	5.0	N 5.0
Carboxymethylcellulose	2.0	2.0	2.0	2.0	1.9	1.7	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.7	2.0	2.0
Cocodiethanolamide	2.0	2.0	2.0	2.0	1.9	1.7	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0	0	1.7	0	0
Sodium Acetate	30	-	-	-	28.8	26.3	-	-	30	30	-	30	30	30	30	30	-	-	21	25	25
Sodium Citrate	17	17	17	-	-	-	-	-	-	-	-	17	17	30	17	17	-	-	16.8	25	25
Sodium Carbonate	-	-	10	10	38.5	35.0	10	-	-	-	-	-	-	-	-	-	-	-	29.4	10	10
Sodium Chloride	-	10	-	10	-	8.8	-	10	-	10	-	-	10	-	-	-	-	-	8.4	10	10
Sodium Sulfate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Trisodium Nitrilotriacetate (NTA)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tergitol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5	-	-	-
Seqlene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sodium Gluconate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gantrez-AN 119	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Weston	-	-	-	-	-	-	-	-	-	-	-	-	-	-	- pH7[e]	- pH9+	-	-	-	-	-
Total Solids[c]	81	61	61	54	100	100	54	54	74	84	44	81	91	94	71	71	32	37	100	97	97
Rank:[d] UST Cloth (57)	4	7	6	2	18	31	14	17	28	38	3	16	30	8	5	21	1	10	25	46	43
EMPA Cloth (56)	35.5	22.5	32	11	30.5	35	26	6.5	6.5	22.5	28.5	27	30.5	36	18	24	20	18	49.5	44	38
Combined Cloth (56)	20	14	25	3	22	33	21	5.5	10	29	16	24	30.5	26	11	17	12	15	43	49	42

Table 4 (cont.)

Components	91	92	93	94	95	96	128	129	130	131	132	133	134	135	136	137	138		
Silicate[b]	10.1	10.1	10.1	10.1	10.1	10.1	5.0	10.1	10.1	5.0	10.1	10.1	10.1	10.1	10.1	10.1	10.1		
Carboxymethylcellulose	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		
Cocodiethanolamide	2.0	2.0	2.0	2.0	2.0	2.0	0	0	0	0	0	0	0	0	0	0	0		
Sodium Acetate	-	-	20	-	-	20	20	-	20	20	30	30	20	-	20	20	20		
Sodium Citrate	-	-	30	-	30	30	20	-	20	20	30	20	20	-	20	20	20		
Sodium Carbonate	-	-	-	-	-	-	15	-	10	10	-	10	-	-	-	10	-		
Sodium Chloride	-	10	-	-	-	-	-	-	-	10	-	-	-	-	-	-	-		
Sodium Sulfate	-	-	-	-	-	-	-	-	-	-	-	-	10	-	-	-	-		
Trisodium Nitrilotriacetate (NTA)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Tergitol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Seqlene	10	10	10	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Sodium Gluconate	-	-	-	10	10	10	15	-	15	10	-	-	10	-	-	-	10		
Gantrez-AN 119	-	-	-	-	-	-	-	1.0	1.0	1.0	-	-	1.0	-	-	-	-		
Weston	-	-	-	-	-	-	-	-	-	-	-	-	-	10	10	10	10		
Total Solids[c]	44	54	94	44	74	94	97	33	98	98	93	92	93	44	92	92	92	Brand	AHAM
Rank:[d] UST	54	55	15	20	19	36	37	53	33	42	26	35	29	9	12	23	24	57	45
EMPA	13	15	37	8	43	47	46	21	54	49.5	48	51	53	42	40	55	45	56	41
Combined	27.5	30.5	37	8	40	48	46	32	54	53	44	52	50	39	38	51	41	56	45

---

[a] All formulations contain 20% surfactant.

[b] "Star" silicate, except as otherwise noted.

[c] Total solids include 20% surfactant; balance = water.

[d] Weighted rank values; Figures in parentheses indicate total number of samples ranked in set: 1 = worst, highest value = best.

[e] Titrated to pH7 with citric acid.

tables. The lettered formulations listed in Table 1 were used with each of the three surfactants while the numbered formulations in Tables 2-4 were used only with the particular surfactant indicated in the heading. Table 5 gives the sources and grades of the formulation components used.

Detergency Evaluation

The relative effectiveness of the formulations was determined on the basis of measuring the reflectivity of the soiled cloth surface before and after washing. A Hunterlab Model D40 reflectometer with green phototube was used for this purpose. The instrument was calibrated against a standard grey tile before each series of measurements. Tests showed that use of the green sensitive phototube avoided interference from the optical brightener contained in the commercial detergent brand used as a reference standard, so that it was unnecessary to use an ultraviolet filter in the light path. Two readings, taken at right angles to each other relative to the warp of the cloth, were made and the detergency values calculated as the average of all the readings taken on the three swatches of the cloth used in the test. In the case of the combined washings, the two types of cloth were evaluated separately.

All the detergency data cited in this report is in reflectance units (RU) expressing the difference in reflectance (R) of the cloth before and after washing. This departure from the previously followed practice of reporting detergency in terms of percent soil removal (%SR) was made for two reasons. It was desired to have as sensitive as possible a means of differentiating between the relative effectiveness of the various formulations but the calculation of the %SR, which involves a multiplication by a factor of 100, tended to magnify any small errors and lack of precision inherent in the method. Secondly, it was realized that, since there is no simple, direct 1:1 relationship between the change of reflectivity and the actual amount of soil removed, the expression of %SR, as previously calculated according to the equation

$$\%SR = (R_w - R_s / R_o - R_s) \times 100$$

where

R_w = Average reflectance of the washed cloth

R_s = Average reflectance of the unwashed soiled cloth

Table 5

FORMULATION COMPONENTS

Component	Source	Specifications
Carboxymethyl-cellulose	Hercules Inc.	Type 7LT
Cocodiethanolamide	Stepan Chemical Co.	Ninol 128 extra
Sodium silicate	Philadelphia Quartz Co.	Solution[a,b]
Sodium acetate	Celanese Chemical Co. (also B&A)	Technical Anhyd., reagent
Trisodium nitrilo-triacetate	Hampshire Chemical Co.	NTA $Na_3 \cdot H_2O$[c]
Sodium carbonate	B&A	Anhyd., reagent
Sodium chloride	B&A	Crystals, reagent
Sodium sulfate	B&A	Anhyd., reagent
Sodium citrate	B&A	Crystals, reagent
Linear alkyl-benzenesulfonate	Conoco	Slurry, C560
Tergitol^{T}[d]	Union Carbide	15-S-9
Seqlene^{T}[d]	Pfanstiehl Labs.	540, Crystals
Sodium d-gluconate	Pfanstiehl Labs.	CP
Gantrez^{T}[d]	GAF	AN-119
Weston^{T}[d]	Borg-Warner	70 S, powder

[a] Two grades were used: "Star" SiO_2/Na_2O ratio = 2.5 and "N" SiO_2/Na_2O ratio = 3.2.

[b] For purpose of formulation their weight percent was calculated on the basis of the solid content of the solution.

[c] Weight percent of components containing water of hydration were calculated in the formulations on the basis of their anhydrous form.

[d] Trademarked products were used "as is" and no corrections in the weight percent in the formulations was made to account for any moisture content.

R_o = Reflectance of the unsoiled cloth

was somewhat misleading.

Although these commercial cloths gave reasonably consistent results throughout each lot (usually 50 yards) purchased, there was occasionally a significant difference in the detergency behavior of different lots. While the initial reflectance values for the soiled cloth for the first two lots of EMPA were very close, the detergency values obtained on these two lots for the AHAM and Brand reference standards were significantly different. For example, at 50 ppm hardness the performance of AHAM is strictly linear and independent of concentration at 44.2 RU on bolt #2 while on bolt #1 the maximum was 39.9 RU at 0.1% and decreased to 36.4 RU at 0.5% concentration. Similar differences are found in the other two hardness grade waters. Figure 4 shows in bar-graph form the differences between these two lots of EMPA cloths. Figures 5-7 show similar differences for AHAM on 6 of the 12 different lots of UST cloth. This variation of behavior of the same type of cloth from bolt to bolt makes the evaluation of soil removal data for the various formulations rather difficult when the formulations to be compared were run on different bolts. With such large differences in soil removal for different lots of the same cloth, it is obvious that both direct comparison of the graphically represented data and the numerical detergency values would be extremely misleading, since both of these comparisons are dependent on the relative ease with which a given bolt is cleaned. Thus, for AHAM on EMPA, for example, in the case illustrated above a detergency value of 36.4 RU does not necessarily imply lower effectiveness of AHAM than does a detergency of 44.2 RU if the first value was obtained on bolt #1 while the second value was obtained on bolt #2 but simply reflects the differences in the soiled cloth itself.

Several statistically valid normalization procedures are available and are frequently used in analytical evaluations where certain data variability can be traced to the presence of one or more non-controllable or non-uniform conditions in the analytical system. The specific technique used depends upon the nature of the data and the kind of non-uniform condition for which data adjustment is required. In our case, this non-uniformity for which data adjustment is required appears to be due to variations in the relative ease of removal of the soil from the cloth which, in turn, is primarily a function of variations in the manufacture of the cloth. The variations in the results obtained with a standard detergent, such as AHAM

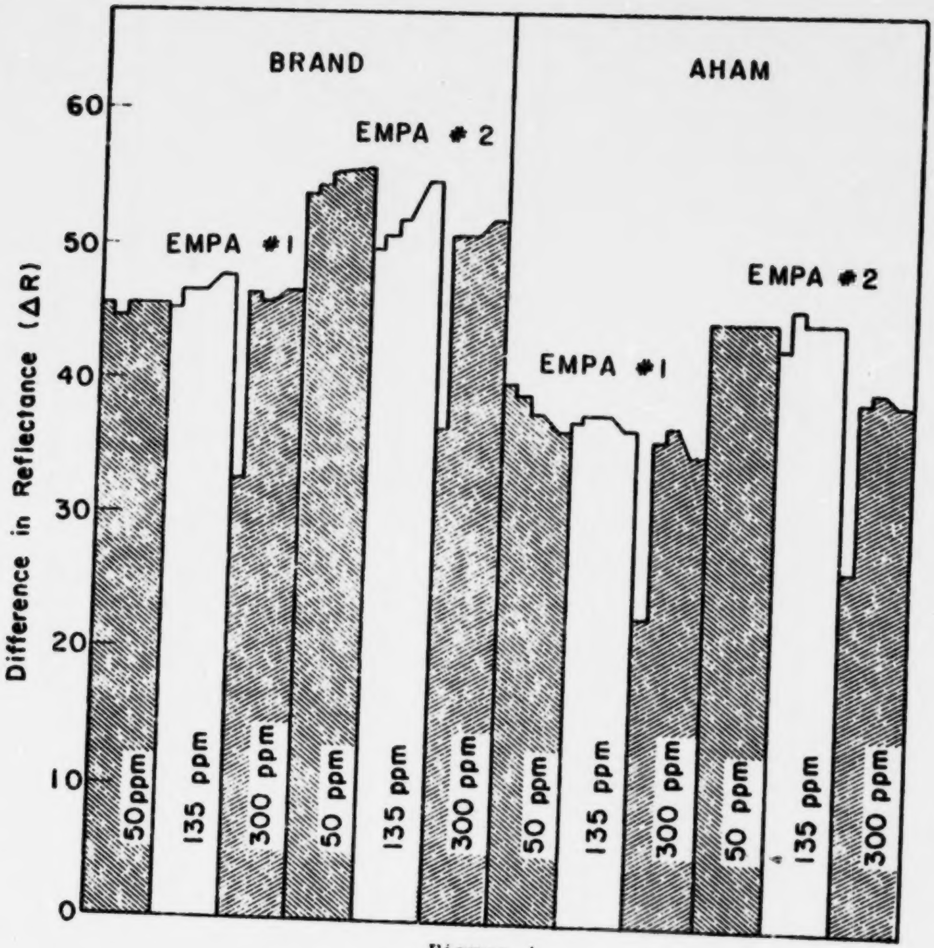


Figure 4
COMPARISON OF TWO BATCHES OF EMPA CLOTH
0.1, 0.2, 0.3 and 0.5% Detergent in Wash Water

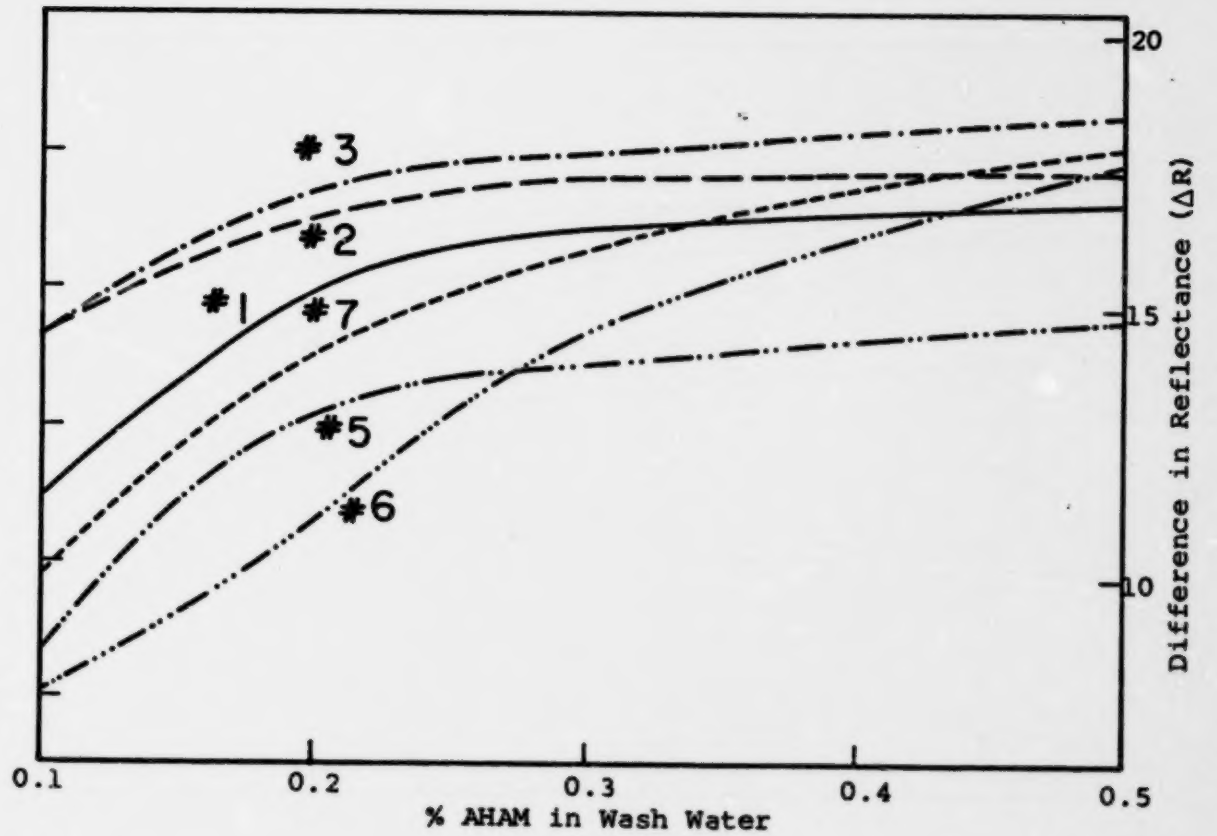


Figure 5

AHAM ON UST CLOTH
50 ppm Hardness Water

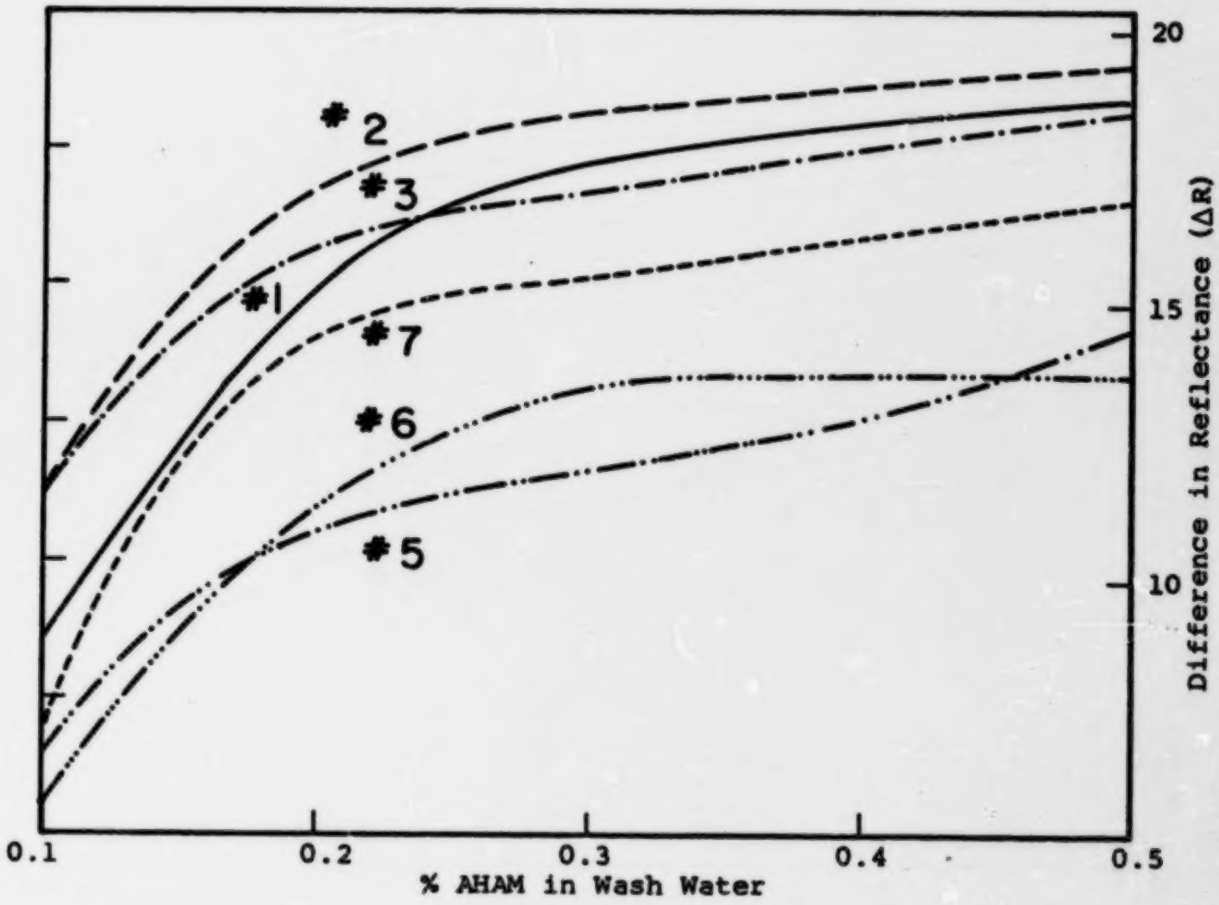


Figure 6
AHAM ON UST CLOTH
135 ppm Hardness Water

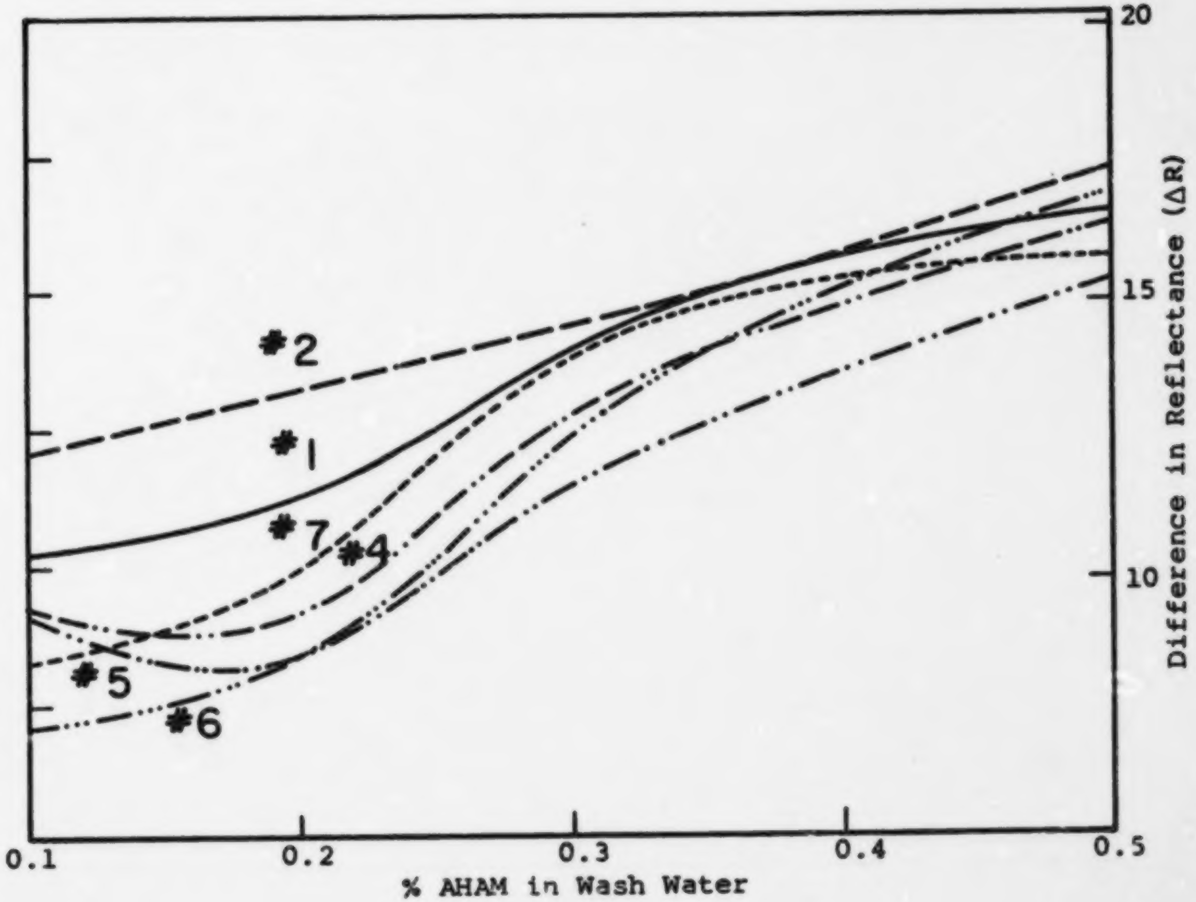


Figure 7

AHAM ON UST CLOTH
300 ppm Hardness Water

or Brand, can be used as an index to the variability of the soiled cloth, since, all other things equal, the differences found with the standard must then represent the differences inherent in the cloth.

Most of the more sophisticated statistical methods of data fitting, such as the Least Mean Square Fit technique, have the disadvantage that they require the use of all the available data. Thus, the process would have had to be repeated, and all previous data readjusted, each time data from a new lot of cloth was added. A number of simpler normalization techniques were therefore tested statistically relative to the detergency data available on this project. While none of the methods gave perfectly matching normalized data, the one described herein yielded data adjustment which was well within the limitations imposed by the precision of the analytical procedure. Usually in such a normalization, one set of control data is assumed as representing "base line" data and the remaining sets of control data are then adjusted relative to this base line. Since a sufficient number of UST lots were available to permit the derivation of a reasonable average, it was decided to use this set of averages as base line data rather than any one of the cloth lots arbitrarily. A normalization factor was then calculated for each lot of cloth by dividing the control values into the base line values thus:

$$\frac{\text{Base Line Value}}{\text{Control Value}_{(\text{lot x})}} = K_{(\text{lot x})}$$

Normalization of the test data was then carried out by multiplying the test results by the applicable normalization factor. It was found that, due to a sensitivity of some cloth lots to both hardness as well as detergent concentration, best data adjustment was obtained by separately calculating the normalization factors for each concentration at each water hardness. The commercial Brand was chosen as the reference detergent, rather than AHAM, because the larger numerical detergency values obtained with it are inherently less affected by small errors in the method. Table 6 illustrates the results of this normalization for the AHAM data for the first nine lots of UST cloth showing both the raw as well as the adjusted data.

A full statistical evaluation of the detergency data to determine trends and specific effects of various formulation components was not within the scope of this project. A simple ranking procedure was, however, used to gain some insight into the relative detergency performance of the various formulations. The procedure used gave relative

Table 6

NORMALIZATION OF UST CLOTH DATA[a,c]
Norm = Average of Brand Control for Lots 1-8

Lot No.	Brand Control Concentration 0.1	0.2	0.3	0.5	Normalization Factors for Concentration 0.1	0.2	0.3	0.5	AHAM Raw Values Concentration 0.1	0.2	0.3	0.5	AHAM Normalized Concentration 0.1	0.2	0.3	0.5
1	Not Available[b]				0.930	0.924	0.966	0.981	10.7	11.7	1[illegible].3	16.7	9.9	10.8	13.8	16.4
2	14.5	18.2	19.6	20.1	0.775	0.800	0.911	0.950	12.5	13.5	14.6	17.4	9.7	10.8	13.3	16.5
3	13.7	18.1	19.3	20.4	0.799	0.820	0.891	0.944	Not Available				Not Available			
4	Not Available[b]				0.995	1.09	1.02	0.975	10.1	9.9	13.5	16.8	10.0	10.8	13.8	16.4
5	9.5	18.6	14.3	18.5	1.10	1.24	1.19	1.06	9.4	8.8	11.7	15.1	10.4	10.9	13.9	16.0
6	8.2	12.0	16.2	18.1	1.33	1.21	1.08	1.04	7.6	8.9	12.5	16.1	10.1	10.8	13.5	16.7
7	9.9	13.8	17.6	19.5	1.11	1.04	0.989	0.990	8.9	10.5	13.7	16.5	9.9	10.9	13.5	16.3
8	9.9	13.4	16.2	18.9	1.10	1.09	1.07	1.03	8.9	9.8	12.8	15.7	9.9	10.7	13.7	16.2
9	12.1	17.5	18.7	20.3	0.901	0.823	0.914	0.946	11.5	13.4	16.8	17.4	10.3	11.7	15.3	16.4
Average	10.9	14.5	17.2	19.2					10.0	10.8	13.8	16.4	10.0	10.8	13.8	16.4

[a] Data for 300 ppm hardness water.

[b] Normalization factors based on AHAM data.

[c] Data, ΔR, is in reflectance units.

rank scores for each of the formulations and could be applied to determine relative performances at any one test condition or overall at any desired combination of test conditions.

The ranking was based on the detergency values which were previously normalized to eliminate differences due to variations in the different lots of cloth. The standard Brand values, which were used as reference data in the normalization step, were included in the data set to be ranked. The formulation having the lowest detergency was assigned a rank value of 1, the next highest a rank of 2, etc. Formulations having identical detergency values were assigned equal rank thus:

Formulation	Detergency	Rank
AX	Lowest	1
....	....	....
XA	10.0	15
XB	10.3	16.5
XC	10.3	16.5
XD	10.5	18
XE	10.7	20
XF	10.7	20
XG	10.7	20
XH	10.8	22
....	....	....
XZ	Highest	N

where

N = total number of samples ranked

This procedure permitted the assignment of equal rank numbers to equal performing formulations while still maintaining the relative positions of the other formulations within the matrix so that the highest ranking sample always had a rank value equal to the total number of samples in the set.

The formulations were ranked separately for each of the 12 test conditions, i.e., 4 concentrations at 3 water hardness levels, used. This gave us an idea as to the relative performance of each formulation with respect to concentration at the different hardness levels.

In order to obtain an approximation of the overall performance of the formulations at each of the 3 hardness levels, the rank values for the 4 concentrations were summed. The formulations were then again ranked on the basis of these sums, thus giving an average rank value for the performance of each formulation with respect to water hardness. Alternatively, the detergency values could have been summed and the ranking done on the average detergencies, but the results would have been just about the same.

Similarly, to obtain the relative overall performance covering all test conditions used, the individual rank values were again summed for each sample and the formulations ranked on the basis of these sums.

The weighted ranking was done by dividing the rank values at each concentration by the appropriate factor: 0.1% = 1, 0.2% = 2, etc., then summing the values and ranking the sums as for overall performance.

A "combined cloth" ranking was done to get a rough idea about the average performance of our formulations relative to the different kinds of soil provided by the two standard cloths. For this, the corresponding detergency values for the two cloths were added before the ranking step was undertaken.

While this ranking system did provide some insights into the relative merits of the various formulations, it should be pointed out that the actual rank values are somewhat less significant than had been hoped. This is particularly true of the rankings of the detergency data for the UST cloth where the performance of most formulations fell within a relatively narrow range so that differences between large numbers of these formulations were of rather little significance. This fact led to low rank values for formulations which nevertheless performed quite well compared to the best ranking formulation. For this reason, it is recommended that the rank data presented here be used with direct reference to the actual detergency data for proper comparison of performance of the formulations.

Results and Discussion

No great benefit can be derived from discussing separately the results of each of the formulations tested during the course of this project. Also, it would be presumptuous to draw any far-ranging conclusions concerning the true practical detergency of these formulations on the basis of bench scale testing on either or both of the particular artificially soiled cloths used for the majority of our evaluations. The following discussion, therefore, is limited to general considerations demonstrating the utility of the candidate surfactants in the development of phosphate-free detergents of a type that avoids many of the problems and hazards of non-phosphated formulations dependent on conventional surfactants.

The weighted overall rank values are included in the tables giving the composition of the formulations (Tables 1-5) and detailed ranking of compound 112A is shown in Tables 7-9, while Tables 10 and 11 give summaries of the rankings for Comp. 112B1 and 212. Detergency values are shown in bar graph form in Figures 8-31 in Appendix A. Figures 8-25 show the performance of the formulations at all the concentrations tested, while Figures 26-43 show the performance at the critical 0.1% concentration which is the use level we would prefer to recommend.

Two events occurring just prior to and shortly after the start of the current program greatly influenced the approach to detergent formulation taken during this project. One was the appearance on the market of several brands of non-phosphated detergents and the other was the suspension of the use of nitrilotriacetate (NTA).

Experience with the non-phosphate products then available pointed up some of the problems encountered with these proprietary formulations. Aside from their high alkalinity, which is undesirable for safety reasons, the high carbonate content of many of these products caused, after several washings, stiffening and/or roughening of the cloth, due to the deposit of the insoluble calcium and magnesium carbonates. We therefore deliberately limited the concentration of sodium carbonate used in our formulations to a maximum of 10% or avoided its use entirely. In fact, we found that with our surfactants a high concentration of carbonate was unnecessary. This is demonstrated by formulations "C" and "CC" which contained 40% and 10% carbonate respectively. For all three surfactants the difference in performance of these two formulations is small. Furthermore, ranking of the formulations indicated

Table 7

DETAILED PERFORMANCE RANKING OF 112A FORMULATIONS
UST Cloth

	No. of Samples	Brand	AHAM	G	A	E	L	C	CC	H	I	II	F	D	J	K	B	N	M	O	24	25	26	32	33	34	35	49	50	51	52	58	59
50 ppm Water Hardness																																	
0.1%	63	51	41	25.5	27	33.5	22	19	49	30.5	33.5	48	28	32	29	33.5	37	39	41	47	13.5	19	41	11	30.5	33.5	43	46	25.5	46	38	54	57
0.2%	63	62	45	42	36	57	18	39	26	61	49.5	27.5	42	56	37.5	42	54.5	51	63	59	19	32	49.5	23	30	27.5	35	33	16	40	34	22	25
0.3%	63	63	55	53.5	47	59	7	52	25.5	60	53.5	21	56	62	45	38	61	29	48	58	33.5	27.5	46	35	36.5	31.5	42	36.5	39	23.5	12	9.5	15
0.5%	63	63	57	41.5	50	53	6	62	21	45	47	14.5	58	60.5	54	41.5	59	3	17	60.5	23	10	35.5	32	31	38	46	19.5	48.5	10	4	19.5	7
135 ppm Water Hardness																																	
0.1%	63	25	5	14	7.5	16	23.5	3	44	17	18	50	11.5	13	55	29	10	27.5	31	47.5	2	11.5	23.5	15	19	20	26	56	27.5	35.5	37	46	42
0.2%	63	50	33	51.5	31	46.5	25	23	20	62.5	57.3	43.5	27	36	62.5	19	38	54	49	30	21	17.5	39	24	33	28.5	37	40.5	6	43.5	45	26	17.5
0.3%	63	58	44.5	60	41	53	28	41	16	62	63	38.5	38.5	50	61	34	41	51.5	59	46.5	32	36	35	20	23	20	25	29	20	44.5	49	17	15
0.5%	63	58.5	52	58.5	50.5	53	24.5	54	11	61	56	16	49	48	63	55	40	35	60	62	39	36	41	23	18	31	20	9	20	29.5	32.5	12	3.5
300 ppm Water Hardness																																	
0.1%	63	23.5	9	13.5	3	13.5	58	22	36.5	26.5	11	33.5	7	6	63	55.5	4	55.5	59	62	1	2	13.5	5	9	9	18.5	38	42	16.5	13.5	25	20.5
0.2%	63	18.5	1	44	2	16	54	6.5	18.5	58	54	48	16	12.5	63	61	11	51	45	62	3.5	3.5	16	10	23.5	14	22	51	20	25.5	25.5	42.5	46.5
0.3%	63	46	16.5	59	21	40.5	31.5	28	5	60	58	55	39	35	62	45	61	29	57	22	16.5	24	18.5	20	24	18.5	26.5	31.5	3	37.5	43.5	30	37.5
0.5%	63	58	39	60.5	43	45	14.5	37	4	62	49	34.5	41	48	52	24.5	63	23	55.5	37	30	34.5	27.5	24.5	26	27.5	30	22	9.5	45	37	14.5	12
Weighted Average Rank																																	
50 ppm	63	63	51	33	32	49	13	28	36	47	44	29	42	50	37.5	40	53	34	48	61	17	20	46	18	26	27	43	45	24	39	25	31	37.5
135 ppm	63	51	33	48	31	43	24	26	23	54.5	52	42	30	36	63	34	32	47	54.5	50	16	20	35	15	19	22	27	38	12	41	45	28	18
300 ppm	63	37	5	47	6	27	45	17	10	56	56	48.5	23	20	63	55	36	44	62	53	1	4	12	2	14	9	21	40	15	34	30	29	32.5
Weighted Overall Rank	63	61	44	41	29	47	18	28	30	52	49	38	33	45	50.5	43	48	39	53	59	13	19	42	14	24	25	37	46	20	36	27	31.5	31.5

Table 7 (cont.)

	60	61	62	72	73	75	76	77	78	79	80	81	101	104	105	111	112	113	114	115	116	118	119	120	121	122	123	124	125	126	127
50 ppm Water Hardness																															
0.1%	16	21	5	52	45	3.5	3.5	8.5	2	53	55	1	23.5	16	23.5	16	63	59	62	61	60	19	11	6.5	13.5	50	58	44	11	8.5	6.5
0.2%	15	20	3	60	37.5	11.5	4	6	2	54.5	47.5	1	7	21	5	13.5	52.5	52.5	58	47.5	44.5	17	8.5	13.5	24	30	46	30	8.5	11.5	10
0.3%	18	23.5	2.5	51	18	18	5	12	1	57	42	2.5	6	21	4	12	50	33.5	30	21	49	44	15	8	40	31.5	42	27.5	25.5	15	9.5
0.5%	25.5	43	1	40	12.5	51.5	33	35.5	10	22	35.5	14.5	8	39	5	51.5	27	12.5	2	17	35.5	55	44	17	56	25.5	29	29	48.5	29	24
135 ppm Water Hardness																															
0.1%	52	40.5	38	45	40.5	33	39	34	33.5	43	58	47.5	32	30	9	21.5	59	60	63	62	61	21.5	4	7.5	49	53.5	57	51	53.5	6	1
0.2%	22	35	16	55.5	40.5	4.5	10.5	12	8	51.5	60.5	9	14.5	13	1	4.5	53	59	60.5	55.5	57.5	14.5	10.5	3	33	28.5	46.5	48	42	7	2
0.3%	10	33	12	56	43	8.5	4	12	2.5	46.5	57	2.5	1	22	5	12	51.5	30.5	54.5	48	54.5	24	7	6	26	18	37	30.5	27	14	8.5
0.5%	9	27.5	2	50.5	34	14	9	15	7	45.5	42.5	3.5	5	20	6	29.5	38	44	57	45.5	47	42.5	26	13	37	1	32.5	27.5	22	24.5	17
300 ppm Water Hardness																															
0.1%	16.5	20.5	23.5	31	33.5	31	31	28.5	28.5	36.5	39.5	41	26.5	18.5	35	51.5	51.5	48.5	60	55.5	51.5	48.5	43.5	43.5	61	46	47	55.5	51.5	39.5	45
0.2%	36.5	49	34	36.5	27.5	38.5	54	32	46.5	59.5	59.5	57	42.5	40.5	5	23.5	34	6.5	40.5	29	51	34	21	8	30.5	27.5	38.5	30.5	56	9	12.5
0.3%	35	43.5	26.5	50	40.5	7	10	9	14	51	48	63	35	13	6	11.5	48	2	56.5	52	53.5	15	11.5	4	42	24	48	33	53.5	1	8
0.5%	32	30	6	50	41	17	2.5	11	5	59	60.5	13	9.5	19	7.5	21	55.5	1	53	54	51	57	16	2.5	33	19	47	41	45	19	7.5
Weighted Average Rank																															
50 ppm	14.5	21	3	60	30	9	4	7	1	58	56	2	11	19	10	16	62	54	55	52	59	23	12	5	22	41	57	35	14.5	8	6
135 ppm	25	37	13	57	44	8	10	14	7	53	60	11	6	17	1	9	58	56	62	59	61	21	4	3	39	29	49	46	40	5	2
300 ppm	32.5	39	19	43	38	24	26	16	25	57	58	50	31	18	3	28	52	8	61	54	59.5	41	22	7	48.5	35	51	42	59.5	11	13
Weighted Overall Rank	16	22	2	58	35	11	6	9	1	56	57	5	12	17	7	15	63	50.5	60	55	62	23	10	3	26	34	54	40	21	8	4

Table 8

DETAILED PERFORMANCE RANKING OF 112A FORMULATIONS
EMPA Cloth

	No. of Samples	Brand	AHAM	G	A	E	L	C	CC	H	I	II	F	D	J	K	B	N	M	O	24	25	26	32	33	34	35	49	50	51	52	58	59
50 ppm Water Hardness																																	
0.1%	59	59	58	2	3	14	8	18	33	6	7	26.5	-	5	56.5	-	-	52	9	56.5	10	-	31	45.5	49	54	29	17	30	21.5	13	15	12
0.2%	59	59	36.5	3	4.5	10.5	32	16	38	9	12	15	-	8	54	-	-	56	18.5	45.5	17	-	24	34	55	47	43	11	25.5	13.5	10	29	35
0.3%	59	57	18	9	1	4.5	10.5	15	35	13	25.5	4.5	-	30.5	56	-	-	58.5	7.5	19.5	19.5	-	29	17	51	45	42	7.5	16	23	27.5	38.5	38.5
0.5%	59	58	12.5	52	11	8	4	18	44	20	22	5	-	39.5	57	-	-	56	6	19	29.5	-	28	14.5	45	25	12.5	7	9	23.5	39.5	43	35.5
135 ppm Water Hardness																																	
0.1%	59	59	58	2	12	11	1	26	26	21	30	9	-	9	46.5	-	-	32	22.5	42	7	-	44.5	30	22.5	37	46.5	28	33	57	38.5	13	3
0.2%	59	59	57	7.5	3	4	20	23	38.5	7.5	15.5	12.5	-	11	58	-	-	41	9	52	17	-	49.5	40	10	27.5	37	35.5	42	21.5	12.5	54	19
0.3%	59	59	43.5	22.5	3	2	20	29.5	47.5	7.5	47.5	14	-	13	58	-	-	54.5	11.5	45	57	-	51.5	34	9	15.5	22.5	25	18.5	29.5	4	41	39
0.5%	59	59	42.5	53	7	2	13.5	40	47.5	16	34.5	18.5	-	24.5	57	-	-	58	18.5	6	44	-	49	22.5	9.5	8	20	31.5	12	9.5	3	28	29.5
300 ppm Water Hardness																																	
0.1%	59	59	52.5	14	5	19.5	1	40	37	16	27	13	-	22.5	32	-	-	17.5	19.5	29	17.5	-	39	24.5	34.5	32	38	10.5	32	22.5	12	2	4
0.2%	59	59	58	14	1	6.5	10	32	51	3	8	19	-	25	46	-	-	42.5	9	31	34	-	30	24	23	33	27.5	17	44.5	6.5	5	22	20.5
0.3%	59	59	45.5	12	1	5	16	21.5	39.5	3	5	15	-	19	57	-	-	39.5	8	53	32	-	42	50.5	48	47	38	11	36	4	9	31	21.5
0.5%	59	59	41	46	1	16	13.5	25.5	32.5	4.5	34	8	-	19.5	57	-	-	58	24	40.5	47.5	-	51	40.5	30.5	42.5	39	15	25.5	4.5	9.5	17	12
Weighted Average Rank																																	
50 ppm	59	59	44	3	1	7.5	10	14	39	4	9	45	-	12	58	-	-	56	5	47	13	-	30	38	54	50	32	7.5	35	18	16	26	24
135 ppm	59	59	55	16.5	2.5	1	6	27	42	8	31	7	-	9	58	-	-	49	12	41	26	-	53	32	10	22	35	29	25	33	14	34	18
300 ppm	59	59	55	19	1	8	5	28	45	3	17	11	-	21	51	-	-	42	14	41	30	-	44	35	33	43	37	10	36	7	4	16	12
Weighted Overall Rank	59	59	49	6	1	4	7	19	40	2	14	11	-	8	58	-	-	55	5	47	17	-	38	37	45	46	35	12	33	20	13	26	22

Table 8 (cont.)

	60	61	62	72	73	75	76	77	78	79	80	81	103	104	105	111	112	113	114	115	116	118	119	120	121	122	123	124	125	126	127
50 ppm Water Hardness																															
0.1%	39.5	25	32	42	11	53	37.5	55	41	19	30	16	26.5	51	39.5	45.5	37.5	43.5	28	1	36	47	21.5	20	48	43.5	4	35	24	34	23
0.2%	33	39	31	49	2	57	51	58	53	6	29	45.5	25.5	44	20.5	48	13.5	36.5	4	7	1	42	27	29	50	23	22	40	20.5	41	52
0.3%	24	21.5	10.5	58.5	2.5	54	41	55	43.5	6	34	51	14	46	32	48	12	47	2.5	27.5	43.5	49	30.5	25.5	51	36.5	21.5	36.5	40	33	53
0.5%	23.5	10	2	59	41	54	49	55	29.5	53	46	51	16.5	48	42	33.5	3	27	47	1	31	37	16.5	14.5	35.5	32	26	38	33.5	21	50
135 ppm Water Hardness																															
0.1%	9	15	5	56	44.5	52	42	38.5	35.5	6	16	14	17.5	48.5	17.5	42	20	48.5	24	54	35.5	53	26	30	55	51	34	4	50	40	19
0.2%	33	24.5	6	49.5	2	27.5	47	53	45	1	14	21.5	24.5	34	43	56	5	32	29	30.5	15.5	55	44	35.5	49.5	38.5	26	18	30.5	46	49.5
0.3%	28	26.5	11.5	38	1	22.5	37	35.5	41	5	6	46	15.5	31.5	56	54.5	7.5	33	35.5	18.5	17	50	43.5	31.5	51.5	41	10	22.5	26.5	49	53
0.5%	21	24.5	11	33	1	38	4.5	54	46	17	36.5	34.5	13.5	42.5	39	56	4.5	51	29.5	31.5	36.5	52	45	22.5	50	55	15	26.5	41	26.5	47.5
300 ppm Water Hardness																															
0.1%	3	7	10.5	28	8.5	58	26	36	8.5	15	21	24.5	30	41	6	52	51	57	43	45.5	47	55	42	49.5	54	49.5	48	45.5	56	34.5	44
0.2%	13	17	11	20.5	4	56	38	50	15	17	29	41	27.5	42.5	2	48	12	57	36.5	35	44.5	54	39	47	52	55	36.5	26	40	49	53
0.3%	26.5	17	10	28.5	2	54.5	41	45.5	19	19	37	52	25	34.5	49	44	7	54.5	23.5	13	14	43	30	26.5	50.5	56	28.5	23.5	33	34.5	58
0.5%	18	28.5	6.5	35	2	53	27	55.5	11	28.5	50	55.5	19.5	30.5	53	38	6.5	47.5	13.5	3	9.5	45	21	22	42.5	36	32.5	23	37	53	49
Weighted Average Rank																															
50 ppm	34	27	25	53	6	55	45	57	46	17	31	33	21	52	37	49	22	43	19	2	29	48	23	20	51	40	11	41	28	36	42
135 ppm	19	20	4	51	11	38	36	50	48	2.5	15	24	16.5	44	39	54	5	47	28	37	23	57	43	30	56	52	21	13	40	46	45
300 ppm	13	15	6	25	2	58	31	49	9	18	32	46	23.5	40	22	50	20	57	26	23.5	29	53	34	39	54	52	38	27	48	47	56
Weighted Overall Rank	29	24	16	51	3	56	43	57	41	10	30	34	21	50	36	52	18	48	23	9	28	53	27	25	54	42	15	32	31	39	44

Table 9

DETAILED PERFORMANCE RANKING OF 112A FORMULATIONS
Combined Cloths

	No. of Samples	Brand	AHAM	Q	A	E	L	C	CC	H	I	II	F	D	J	K	B	N	M	O	24	25	26	32	33	34	35	49	50	51	52	58	59
50 ppm Water Hardness																																	
0.1%	59	59	58	2	3	16	4.5	13	44	8	10.5	37.5	-	7	56	-	-	53.5	19	57	6	-	36	28	43	51	34.5	39	45.5	30	23	33	34.5
0.2%	59	59	48	5	3.5	42	21	27.5	37	37	27.5	13.5	-	24	55.5	-	-	58	49.5	55.5	10	-	44	29	54	46.5	49.5	11	16.5	25.5	13.5	22.5	33
0.3%	59	59	43	28.5	9	28.5	2	37.5	30	39	46	4	-	52.5	57	-	-	56	12.5	46	23	-	41	23	51	41	46	7.5	26	17	15	21	26
0.5%	59	59	38	53	25.5	25.5	2.5	48.5	34.5	30.5	36	4	-	54	58	-	-	48.5	5	46.5	20.5	-	33	11	39	30.5	20.5	6.5	20.5	10	16	32	15
135 ppm Water Hardness																																	
0.1%	59	59	47	1	5	9.5	2	8	36.5	12	16.5	29.5	-	6	49	-	-	22.5	22.5	44	3	-	28	13.5	15	21	31	45	24	56	38.5	29.5	18
0.2%	59	59	56	29	3	7.5	16	15	32	41.5	39	20.5	-	14	58	-	-	55	23.5	50	7.5	-	53	34	12	26.5	46	47	18	34	20.5	48.5	10
0.3%	59	59	50	52	4	6.5	23	42	33	48	57	29.5	-	40	58	-	-	56	44.5	51	54	-	49	23	6.5	9	19	27	11.5	46	13.5	29.5	23
0.5%	59	58	50	57	30	9.5	17	53.5	31	49	53	14.5	-	37.5	59	-	-	56	47.5	40	41	-	47.5	23.5	8	14.5	19	20	11	14.5	5	21.5	9.5
300 ppm Water Hardness																																	
0.1%	59	56.5	40	10.5	3	16.5	2	33	35.5	20	21.5	18	-	14	50	-	-	38	39	46	5	-	31	14	24	23	27.5	16.5	35.5	19	7.5	λ	6
0.2%	59	59	39.5	21	1	3	17.5	14	42	11	9	24.5	-	11	58	-	-	50	7.5	48.5	14	-	21	7.5	17.5	27.5	21	27.5	38.5	6	4.5	27.5	24.5
0.3%	59	59	42	41	1	7	19	19	13.5	13.5	21	36.5	-	23	57	-	-	49.5	26.5	53	17	-	39.5	49.5	51	43.5	45	11	9.5	4.5	12	38	26.5
0.5%	59	59	52	56	2	29.5	6.5	33.5	11	27	44	16.5	-	36.5	58	-	-	54	45	47.5	47.5	-	50.5	33.5	23	40	36.5	12.5	12.5	15	20	8.5	5
Weighted Average Rank																																	
50 ppm	59	59	53	8	1	28	2	26	44	20	21	19	-	24	58	-	-	57	23	56	6	-	42	29	50	49	41	22	35	25	15	31	32
135 ppm	59	59	55	32	3	2	7	27	37	40	43	25	-	19.5	58	-	-	49	35	51	22.5	-	47	21	5	14	31	42	11	44	18	36	9
300 ppm	59	59	47	32.5	1	8	5.5	22.5	26.5	12	18	20	-	16	58	-	-	52	30	54	15	-	37	22.5	29	35	34	11	21	7	4	14	9
Weighted Overall Rank	59	59	54	11	1	14.5	3	24	38	21	29	19	-	20	58	-	-	57	28	56	7	-	46	22	43	45	37	25	33	27	10	32	26

Table 9 (cont.)

	60	61	62	72	73	75	76	77	78	79	80	81	103	104	105	111	112	113	114	115	116	118	119	120	121	122	123	124	125	126	127
50 ppm Water Hardness																															
0.1%	25	15	17	47	24	41	21	49	21	37.5	45.5	4.5	18	42	26	29	55	53.5	50	1	52	31.5	12	9	31.5	48	27	40	14	21	10.5
0.2%	16.5	30	7	57	2	51	31.5	53	31.5	20	45	19	8	40.5	3.5	37	34.5	52	13.5	18	1	34.5	9	13.5	46.5	25.5	39	43	6	27.5	40.5
0.3%	15	15	1	58	3	50	12.5	54.5	11	23	41	32.5	5	37.5	7.5	36	26	46	6	19.5	49	52.5	18	10	54.5	35	34	31	32.5	19.5	46
0.5%	17	13	1	56	25.5	57	46.5	55	13	50	42	40	8	45	18	44	6.5	13	23	2.5	34.5	51	25.5	9	52	28.5	28.5	37	42	20.5	42
135 ppm Water Hardness																															
0.1%	33	26	16.5	57	41.5	41.5	40	36.5	35	19.5	43	32	19.5	34	7	26	46	54	50	58	53	38.5	9.5	11	55	52	48	26	51	13.5	4
0.2%	31	29	2	57	5	5	29	37	23.5	1	43	5	10	18	13	36	23.5	54	52	51	39	44	26.5	10	48.5	39	41.5	34	45	23.5	18
0.3%	9	35.5	2	55	3	5	11.5	16	15	13.5	38	17	1	20.5	33	38	35.5	38	53	42	47	42	18	9	44.5	29.5	20.5	25.5	25.5	33	29.5
0.5%	7	25	2.5	44	1	26.5	4	37.5	28.5	32	42	14.5	6	33.5	23.5	46	12	53.5	51	39	44	53.5	36	18	44	2.5	21.5	28.5	33.5	26.5	35
300 ppm Water Hardness																															
0.1%	4	7.5	9	27.5	14	58	25	32	10.5	21.5	26	29.5	29.5	35.5	12	53	52	59	50	47.5	50	54	41	43	55	44	45	47.5	56.5	35.5	42
0.2%	16	27.5	11	19	4.5	57	47	52	23	33.5	42	52	31.5	44.5	2	44.5	14	46	39.5	35	52	56	31.5	33.5	54	55	38	30	48.5	36.5	42
0.3%	32.5	30	8	48	2	34.5	19	23	4.5	39.5	55	58	32.5	16	23	26.5	15	26.5	46.5	30	34.5	36.5	9.5	3	56	54	46.5	30	52	6	43.5
0.5%	22	24.5	3	50.5	1	40	8.5	38	4	53	57	40	10	18.5	31	24.5	27	16.5	33.5	18.5	27	55	14	6.5	47.5	21	42.5	33.5	47.5	42.5	29.5
Weighted Average Rank																															
50 ppm	16	13	4	55	10	51	27	54	17	36	48	12	7	47	11	37	45	52	33	3	38	39	9	5	46	40	34	43	14	18	30
135 ppm	19.5	30	1	57	8	16	24	34	26	10	46	13	4	28	12	41	33	54	56	52.5	50	48	17	6	52.5	38	39	29	45	22.5	15
300 ppm	13	17	3	38	2	53	25	41	5.5	39.5	49	50.5	26.5	31	10	42	28	43	47	36	45	55	24	19	57	50.5	47	39.5	56	32.5	44
Weighted Overall Rank	13	17	2	55	6	49	23	52	16	34	50	14.5	5	42.5	8.5	36	39.5	53	41	12	47	48	8.5	4	51	44	35	39.5	30	18	31

Table 10

SUMMARY OF PERFORMANCE RANKING OF COMPOUND 11281 FORMULATIONS

	No. of Samples	Brand	AHAM	G	A	E	L	C	CC	H	I	II	F	D	J	K	B	M	N	O	20	21	22	36	37	38	39	40	41
0.1% Concentration on UST Cloth at																													
50 ppm	53	49	44	19.5	26	39	2.5	10.5	40	31.5	35.5	46	16	25	14	17.5	37	31.5	50	22	10.5	1	27	47	48	34	28.5	5.5	2.5
135 ppm	53	28	6	5	12.5	19.5	32	5	39.5	14	15	49.5	9	7	23.5	26	26	35	16	43	4	2	1	23.5	21.5	32	26	36	37
300 ppm	53	31.5	18	18	15.5	20.5	36.5	6.5	2	28.5	11.5	46	23.5	4	44	47	11.5	43	40.5	48	3	6.5	5	8	28.5	23.5	15.5	33.5	40.5
on EMPA Cloth at																													
50 ppm	47	47	46	5	4	23	23	9.5	13	9.5	2	27	43	7.5	-	-	-	11	3	45	-	-	-	29	28	36	39	30	34
135 ppm	47	47	46	19	7	19	27	44	24	19	14	42	34	10	-	-	-	30	25.5	22	-	-	-	28	35.5	40	41	29	6
300 ppm	47	47	45	17.5	11	25.5	37	42	34.5	25.5	15	44	24	17.5	-	-	-	39	21	12	-	-	-	20	27	36	32	40	29
on Combined Cloth at																													
50 ppm	47	47	43.5	2.5	4	24	9.5	1	18.5	9.5	5	29.5	44	7	-	-	-	11.5	18.5	45	-	-	-	34	32	29.5	36.5	22	23
135 ppm	47	47	45	5	6	13	23	41	25.5	9	9	43	16	3.5	-	-	-	32	16	25.5	-	-	-	19.5	33	38	39.5	30.5	11
300 ppm	47	46	40	15	11.5	23.5	36	37	18.5	25.5	11.5	42	22	6.5	-	-	-	39	27	29	-	-	-	13.5	25.5	30.5	28	38	32.5
Weighted Ranking on UST Cloth at																													
50 ppm	53	53	51	28	38	47	2	25	32	44	37	36	30	41	24	22	50	26	52	35	10	5	31	46	43	30	29	9	8
135 ppm	53	51	28	42	26	41	17.5	22	43	46	45	44	19	29	25	20	32	30	38.5	40	11	10	9	33	23.5	23.5	12.5	15	31
300 ppm	53	43.5	13	46.5	34	27	37	12	7	50	39.5	49	30	18.5	43.5	46.5	27	35	23	38	6	2	3	21	32	20	15	8	17
on EMPA Cloth at																													
50 ppm	47	47	40	3	1	16	35	4	12	6	2	21	36	11	-	-	-	5	10	39	-	-	-	31	27	43	44	29	24
135 ppm	47	47	45	6	1	12	30	31	11	8	5	33	27	19	-	-	-	9	32	29	-	-	-	20	25	42	43	28	10
300 ppm	47	47	45	5	1	15.5	17	36	31	15.5	4	44	12	22	-	-	-	29	19	13	-	-	-	24	28	38	37	43	27
on Combined Cloth at																													
50 ppm	47	47	46	1	2	19	21	4	13	10	3	20	43	16	-	-	-	6	27	45	-	-	-	39	31	37	42	25	15
135 ppm	47	47	46	6	2	13	25	36	10	21	5	40	23	26	-	-	-	9	35	34	-	-	-	19	33	43	41	17	12
300 ppm	47	47	42	5	2	16.5	21	36	14	34.5	4	44	13	18	-	-	-	30	12	19.5	-	-	-	22	29	38	37	34.5	15
Weighted Overall Rank on																													
UST Cloth	53	53	46.5	32	35	45	5	24	31	48	41	40	27.5	34	27.5	26	46.5	29	50.5	37	7.5	3	21	39	36	30	22	9	12
EMPA Cloth	47	47	45	3	1	16	34	11	12	6	2	25	33	13	-	-	-	8	17	36	-	-	-	27	28	42	43	31	22
Combined Cloths	47	47	46	2	1	18	19	11	12	13	3	27	39	17	-	-	-	9	25	45	-	-	-	33	32	41	43	22	15

Table 10

SUMMARY OF PERFORMANCE RANKING OF COMPOUND 11281 FORMULATIONS

	No. of Samples	Brand	ANAM	O	A	B	L	C	CC	H	I	II	F	D	J	K	S	E	N	G	20	21	22	36	37	38	39	40	41
0.1% Concentration on UST Cloth at																													
50 ppm	53	49	44	19.5	26	39	2.5	10.5	40	31.5	35.5	46	16	25	14	17.5	37	31.5	50	22	10.5	1	27	47	48	24	30.5	5.5	2.5
135 ppm	53	28	6	5	12.5	19.5	32	5	39.5	14	15	49.5	9	7	23.5	26	26	35	16	43	4	2	1	23.5	21.5	32	26	36	37
300 ppm	53	31.5	18	18	15.5	20.5	36.5	6.5	2	28.5	11.5	46	23.5	4	44	47	11.5	43	40.5	48	3	6.5	5	8	28.5	33.5	15.5	33.5	40.5
on EMPA Cloth at																													
50 ppm	47	47	46	5	4	23	23	9.5	13	9.5	2	27	43	7.5	-	-	-	11	3	45	-	-	-	29	29	36	39	30	34
135 ppm	47	47	46	19	7	19	27	44	24	19	14	42	34	10	-	-	-	30	25.5	23	-	-	-	28	35.5	40	41	29	6
300 ppm	47	47	45	17.5	11	25.5	37	42	34.5	25.5	15	44	24	17.5	-	-	-	39	21	12	-	-	-	20	27	36	32	40	29
on Combined Cloth at																													
50 ppm	47	47	43.5	2.5	4	24	9.5	1	18.5	9.5	5	29.5	44	7	-	-	-	11.5	18.5	45	-	-	-	34	32	29.5	36.5	22	23
135 ppm	47	47	45	5	6	13	23	41	25.5	9	9	43	16	3.5	-	-	-	32	16	25.5	-	-	-	19.5	33	38	39.5	30.5	11
300 ppm	47	46	40	15	11.5	23.5	36	37	18.5	25.5	11.5	42	22	6.5	-	-	-	39	27	29	-	-	-	13.5	25.5	30.5	28	30	32.5
Weighted Ranking on UST Cloth at																													
50 ppm	53	53	51	28	38	47	2	25	32	44	37	36	30	41	24	22	50	26	52	35	10	5	31	46	43	20	29	9	0
135 ppm	53	51	28	42	26	41	17.5	22	43	46	45	44	19	29	25	20	32	30	38.5	40	11	10	9	33	23.5	23.5	12.5	18	31
300 ppm	53	43.5	13	46.5	14	27	37	12	7	50	39.5	49	30	18.5	43.5	46.5	27	35	23	38	6	2	3	21	32	20	15	8	17
on EMPA Cloth at																													
50 ppm	47	47	40	3	1	16	35	4	12	6	2	21	36	11	-	-	-	5	[illegible]	39	-	-	-	31	27	43	44	29	24
135 ppm	47	47	45	6	1	12	30	31	11	8	5	33	27	19	-	-	-	9	[illegible]	29	-	-	-	20	25	42	43	28	10
300 ppm	47	47	45	5	1	15.5	17	36	31	15.5	4	44	12	22	-	-	-	29	[illegible]	13	-	-	-	24	28	38	37	43	27
on Combined Cloth at																													
50 ppm	47	47	46	1	2	19	21	4	13	10	3	20	43	16	-	-	-	6	27	45	-	-	-	39	31	37	42	25	15
135 ppm	47	47	46	6	2	13	25	36	10	21	5	40	23	28	-	-	-	9	35	34	-	-	-	19	33	43	41	17	12
300 ppm	47	47	42	5	2	14.5	21	36	14	34.5	4	44	13	18	-	-	-	30	12	19.5	-	-	-	22	29	38	37	34.5	15
Weighted Overall Rank on																													
UST Cloth	53	53	46.5	32	35	45	5	24	31	48	41	40	27.5	34	27.5	26	46.5	29	50.5	37	7.5	3	21	39	36	20	22	9	12
EMPA Cloth	47	47	45	3	1	16	34	11	12	6	2	25	33	13	-	-	-	8	17	36	-	-	-	27	28	42	43	31	22
Combined Cloths	47	47	46	2	1	18	19	11	12	13	3	27	39	17	-	-	-	9	25	45	-	-	-	33	32	41	43	22	15

Table 10 (cont.)

	63	64	65	66	67	70	71	82	83	84	85	86	87	88	97	98	99	100	101	102	106	107	108	109	110
0.1% Concentration on UST Cloth at																									
50 ppm	8	15	22	4	38	43	31.5	12	8	42	45	41	31.5	34	22	8	28.5	35.5	19.5	17.5	50	5.5	13	52	53
135 ppm	51	45	48	46.5	46.5	44	29.5	29.5	12.5	41	32	21.5	18	38	39.5	8	41.5	10.5	10.5	19.5	49.5	34	17	52.5	52.5
300 ppm	31.5	20.5	14	11	23.5	30	18	11.5	23.5	1	27	36.5	26	36.5	42	8.5	45	33.5	36.5	39	52	49	50.5	50.5	53
on EMPA Cloth at																									
50 ppm	20.5	38	25	14	16	26	17.5	42	40	12	7.5	6	1	36	36	23	32.5	32.5	31	41	20.5	15	44	19	17.5
135 ppm	8.5	19	11	13	15.5	43	38	39	32.5	5	4	2	1	8.5	15.5	3	25.5	23	45	32	11.5	35.5	37	31	19
300 ppm	15	13	2	8	7	23	19	9.5	22	6	4	5	3	15	9.5	1	28	32	30	34.5	38	41	46	43	32
on Combined Cloth at																									
50 ppm	13	27	20	6	21	25.5	16.5	41	36.5	16.5	15	11.5	2.5	34	28	14	31	34	25.5	42.5	39.5	8	42.5	[illegible]	39.5
135 ppm	30.5	28	19.5	23	28	45.5	36.5	36.5	16	12	7	3.5	2	14	18	1	28	9	44	21	23	35	34	42	39.5
300 ppm	17	13.5	3	6	8	23.5	16	9.5	20.5	2	5	9.5	4	18.5	20.5	1	34.5	32.5	30.5	34.5	44	43	47	45	41
Weighted Ranking on UST Cloth at																									
50 ppm	14	21	34	3	18	33	17	7	4	42	39	45	27	23	11.5	1	15	19	13	11.5	49	6	16	40	48
135 ppm	34	37	35.5	27	12.5	50	17.5	8	3	47.5	47.5	35.5	38.5	21	14	1	16	4	2	6	49	7	5	52	53
300 ppm	39.5	29	25	22	14	41.5	16	4.5	4.5	31	41.5	48	36	24	18.5	1	33	10	11	9	52	45	27	53	51
on EMPA Cloth at																									
50 ppm	33	37	32	14	15	23	13	46	45	19	9	7	8	28	26	18	30	34	38	42	20	25	41	22	17
135 ppm	26	34	22	21	17	35.5	16	44	37	13	7	3	2	24	14	4	38	39	46	41	15	40	35.5	18	23
300 ppm	26	25	8	7	10	21	6	14	32	11	9	3	18	34	33	2	35	39	40	41	30	42	46	20	23
on Combined Cloth at																									
50 ppm	28	33	34	5	12	22	9	44	38	23	14	11	7	26	18	8	24	29	30	40	36	17	41	32	35
135 ppm	38	42	29.5	18	8	45	11	39	15	22	14	4	3	24	7	1	29.5	20	37	31	27	28	16	32	44
300 ppm	27	25.5	10	7.5	7.5	31	3	6	11	19.5	16.5	9	23	28	25.5	1	39	24	32	33	46	40	45	41	43
Weighted Overall Rank on																									
UST Cloth	19	23	33	6	16	38	17	4	2	43	42	44	30	25	13	1	18	14	10	11	50.5	7.5	15	49	52
EMPA Cloth	30	37	26	14	15	24	9	46	39	18	7	4	5	29	23	10	35	38	41	44	20	32	40	21	19
Combined Cloths	29	36	31	7	10	26	6	44	30	21	14	8	5	23	16	4	24	28	34	38	37	20	40	35	42

Table 11

SUMMARY OF PERFORMANCE RANKING OF COMPOUND 212 FORMULATIONS

	No. of Samples	Brand	AHAM	G	A	E	L	C	CC	H	I	II	F	D	J	K	B	N	M	O	28	29	30	31	42	43	44	45	46	47	48
0.1% Concentration on UST Cloth in																															
50 ppm	57	54	50	42	21	43.5	14.5	41	10.5	52	36	17	22	45.5	48	39	28	47	45.5	50	3	4	7.5	2	27	39	10.5	7.5	9	26	5.5
135 ppm	57	37	21	31	18.5	27.5	34	24.5	7	24.5	10.5	7	27.5	16.5	35	40	23	26	33	36	4.5	3	7	1	32	39	16.5	9	20	15	4.5
300 ppm	57	41	37	35	24	29.5	27.5	39	5.5	32.5	31	5.5	22.5	29.5	42	34	19.5	27.5	32.5	37	12.5	4	17	8	21	25.5	18	2	2	10.5	2
on EMPA Cloth in																															
50 ppm	56	56	54	1	8	27	11	17	9	10	4	14.5	55	2	42	45	-	14.5	22	43	26	21	25	3	31	36	20	5	7	24	23
135 ppm	56	56	52	1	5	17	13.5	33	6	7	4	11	34	3	24.5	24.5	-	11	27.5	41	27.5	22	30.5	2	40	42	26	15	13.5	16	9
300 ppm	56	55	51	5.5	18.5	9.5	9.5	37	2.5	16	14	7	26	2.5	22	23.5	-	5.5	31	39	26	12.5	29	1	36	42	23.5	12.5	4	20	11
on Combined Cloths in																															
50 ppm	56	56	55	1	9.5	27	11	20.5	6	18	9.5	13	54	5	43	45	-	20.5	25	49.5	17	12	19	2	31	38	14	3	4	22	15.5
135 ppm	56	53.5	40	4	7	21	23	31	5.5	14.5	2.5	9.5	32	2.5	30	33	-	17	29	37	22	14.5	25	1	35	38	24	11	12	5.5	9.5
300 ppm	56	55	43	22.5	24	22.5	20.5	36.5	3	28	25.5	4.5	25.5	18	30	29	-	17	32	36.5	15	6.5	20.5	1.5	33	35	16	6.5	1.5	4.5	12.5
Weighted Ranking on UST Cloth in																															
50 ppm	57	57	50	44	29	48.5	9	46	16	56	31	22.5	34	55	52	40	42	43	47	51	5	8	6	1	20	33	12	18	28	37	33
135 ppm	57	56	35	55	23	50	33	43	38	53	44	27	20	24	45	33	43	21	54	29	2	5	9	3	13	22	28	30	46	47	10
300 ppm	57	50	26.5	49	20	37.5	35	42	11.5	51.5	23	14	30	39.5	51.5	43	11.5	25	28	39.5	24	21	15	6	13	16.5	26.5	5	9	16.5	4
EMPA Cloth in																															
50 ppm	56	56	39	2	7	30	12	13	10	8	3	11	55	1	27	36	-	19	16	41	33	20	29	9	24	31	26	6	5	23	34
135 ppm	56	56	45	1	3	16	23	25	5	7	4	6	49.5	5	29	24	-	21	20	39	32	22	38	9	35	37	27	14	12	18	19
300 ppm	56	56	50	1	3	12	16	38	13	6	5	8	33	2	29.5	26	-	18	22	34	32	28	37	14.5	35.5	41	31	4	7	20	10.5
Combined Cloth in																															
50 ppm	56	56	45	1	9	38	5	15	7.5	22	7.5	10	55	2	34	39	-	24	25	51	23	12	20.5	3	20.5	33	19	6	11	32	18
135 ppm	56	56	48.5	3	6	27	27	23.5	4	18	10	7	48.5	1	39	25	-	23.5	29.5	41	14	11	34	5	32	35	27	14	14	29.5	16
300 ppm	56	56	41	11	5	23.5	23.5	40	9.5	19	12	6.5	38	9.5	35	26.5	-	21	22	36	30	25	31	13	28.5	32	26.5	1	4	15.5	8
Weighted Overall Ranking on																															
UST Cloth	57	57	45	48	27	50.5	11	44	13	56	34	22	32	50.5	52	41	40	39	47	49	4	7	6	2	18	31	14	17	28	38	3
EMPA Cloth	56	56	41	1	4	25	12	14	9	5	3	10	52	2	28.5	33.5	-	18	16	39	33.5	22.5	12	11	30.5	35	26	6.5	6.5	22.5	28.5
Combined Cloths	56	56	45	1	7	34	13	19	4	18	5.5	9	55	2	35	36	-	23	27.5	47	20	14	25	3	22	33	21	5.5	10	29	16

Table 11 (cont.)

	53	54	55	56	57	68	69	74	89	90	91	92	93	94	95	96	128	129	130	131	132	133	134	135	136	137	138
0.1% Concentration on UST Cloth in																											
50 ppm	34	50	16	12.5	33	1	18.5	18.5	53	32	55	56	14.5	24	20	31	36	57	36	43.5	24	39	30	5.5	12.5	24	29
135 ppm	13.5	10.5	22	12	18.5	2	13.5	29.5	45	48	38	42	57	29.5	41	49	51	44	52	55	46	53	54	50	43	56	47
300 ppm	15	8	8	12.5	14	10.5	16	25.5	57	55	45	44	22.5	19.5	37	47.5	50	40	56	53	50	54	52	43	29	47	50
on EMPA Cloth in																											
50 ppm	32.5	32.5	37	26	29	12	17	53	47	40	13	19	39	6	38	49.5	41	17	51	46	44	48	49.5	30	34	52	35
135 ppm	8	23	32	21	18	19	30.5	55	48	38	20	29	35	11	36	43	44	45	47	50	51	53	46	39	37	49	45
300 ppm	16	16	21	8	18.5	26	28	56	49	44	34	35	33	30	40	46	48	32	54	52	50	53	47	41	44	38	44
on Combined Cloths in																											
50 ppm	36	39	33	24	28	8	15.5	45	53	40	26	29.5	34	7	36	47	41.5	29.5	52	49.5	41.5	49.5	45	23	32	49.5	36
135 ppm	9.5	20	28	18	16	8	26	44	45.5	41	27	34	56	19	36	43	47	53.5	49	51	50	55	48	42	39	52	45.5
300 ppm	12.5	9	10.5	8	12.5	14	18.5	53	54	49	39.5	39.5	31	27	38	45.5	47.5	34	56	51	50	52	47.5	42	44	41	45.5
Weighted Ranking on UST Cloth in																											
50 ppm	22.5	39	10	7	25	2	13	27	45	38	53	54	14	15	17	32	35	48.5	30	41	21	36	26	4	11	19	24
135 ppm	6	11	7	4	18.5	1	8	16	31	49	51	52	17	48	14	41	39	57	33	41	25	41	36	37	12	26	18.5
300 ppm	19	7	9	2.5	9	1	2.5	22	57	54	55	56	31	18	32	48	44.5	53	44.5	41	36	37.5	46	47	34	33	29
EMPA Cloth in																											
50 ppm	32	28	35	18	22	25	21	50	44	38	14	15	40	4	43	48	47	17	53	49	46	52	51	45	37	54	42
135 ppm	10.5	31	33	26	28	8	13	41	46	36	15	17	34	10.5	44	43	42	30	49.5	51	55	47	54	40	48	53	52
300 ppm	21	25	29.5	10.5	19	9	14.5	54	43	40	23	24	35.5	17	42	45	52.5	27	55	44	52.5	46	47	39	48	49	51
Combined Cloth in																											
50 ppm	31	30	27	13	17	16	14	46	49	42	26	29	36	4	40	48	44	28	54	53	43	52	47	37	35	50	41
135 ppm	8	31	22	12	20	2	9	36	43	44	17	21	33	19	37	45.5	45.5	38	51	52.5	54	50	55	42	40	52.5	47
300 ppm	17	18	20	3	14	2	6.5	49	54	46	34	33	37	15.5	39	48	53	28.5	55	45	51	44	51	42.5	47	51	42.5
Weighted Overall Ranking on																											
UST Cloth	16	30	8	5	21	1	10	25	46	43	54	55	15	20	19	36	37	53	33	42	26	35	29	9	12	23	24
EMPA Cloth	27	30.5	36	18	24	20	18	49.5	44	38	13	15	37	8	43	47	46	21	54	49.5	48	51	53	42	40	55	45
Combined Cloths	24	30.5	26	11	17	12	15	43	49	42	27.5	30.5	37	8	40	48	46	32	54	53	44	52	50	39	38	51	41

that only with compound 212 did the use of carbonate appear to have any beneficial effect.

The discontinuance of the use of NTA completely eliminated this compound from consideration as a component in any of our formulations during the present project even though earlier experiments (formulations F, J, K and O) had indicated that NTA could significantly enhance the performance of all three of our surfactants. Formulations "J" and "O" were among the top ranking formulations with compounds 112A and 212. Word that the use of NTA was being reconsidered came too late to resume testing of NTA under this project. Although we continue to view the use of NTA with some reservations, primarily because nitrogen content can possibly be made available as a plant nutrient and hence contribute to eutrophication, we would recommend that further formulations of our candidate surfactants containing limited concentrations of NTA be bested for detergent efficiency.

One of the difficulties in deriving any significant behavior pattern for our candidate surfactants stems from the fact that many of the formulations tested exhibited large differences in their detergency on the two cloths. Although the EMPA cloth appears to be much easier to clean, the detergency values falling into the 40-50 RU range for the "Brand" standard and 35-45 RU for the AHAM, as compared to the UST cloth where detergencies ranged from 10-20 RU for both standards, the relative performance of our surfactants appears to be less favorable on that cloth than on the latter cloth. While generally most formulations which ranked high on the UST cloth also rank high on EMPA, many formulations, e.g., 112A-78, 112A-M, did show large differences in their relative rank on the two cloths. This was particularly true at the 0.1% concentration. Compound 212 was somewhat less susceptible to the differences in the two cloths than either 112A or 112B1.

Some trends did, however, emerge. For example, the addition of sodium citrate to formulations in most cases markedly enhanced the detergency on the EMPA cloth with both compounds 112A and 212, although its contribution to the effectiveness of these formulations on UST cloth was negligible. Lowering the alkalinity of the formulations by decreasing the amount of silicate or substituting "N" grade silicate for the "Star" grade further enhanced this effect with these two surfactants. Addition of electrolytes, especially sodium chloride, further improved the performance of many of these formulations. On the other hand, the use of citrate in formulations with surfactant

112B1 appeared to have no significant effect on the detergent efficiency. Surprisingly, the addition of Tergitol 15-S-9 had relatively little effect on improving the performance of our surfactants. We had added the nonionic surfactant in the hopes of achieving a synergistic effect by improving the removal of nonpolar soil components which the Tergitol should have been a somewhat better solubilizer for. This did not seem to be the case.

Formulations 112A-73, 112B1-71, 112B1-98 and 212-29 which contain Tergitol are directly comparable to formulations 112A-72, 112B1-70, 112B1-97 and 212-68 respectively, which do not contain the nonionic surfactant. In all of these formulations, we dropped the use of cocodiethanolamide (CDA) because we felt that this foam supressant was not required with our surfactants. In fact, it turned out that these formulations without the CDA were significantly superior to formulation "A" to which they are also directly comparable. This effect is particularly noticeable on the EMPA cloth.

One of the shortcomings of surfactant 212, its relatively poor performance at the very low concentration level (0.1%), was partially overcome by the use of "N" grade sodium silicate. This grade of silicate differs from the "Star" grade in the ratio of SiO_2 to Na_2O and in the relative pH. The SiO_2/Na_2O ratio for the "N" grade is 3.22 while that for the "Star" is 2.5 and the pH is lower in solutions of equivalent concentration for the "N" grade than that for the "Star." Both grades were supplied by the Philadelphia Quartz Co. Although the overall performance of the formulations, 212-53 to 212-55, using the "N" silicate was not significantly better than that of similar formulations using the "Star" silicate, their effectiveness at the 0.1% detergent formulation in the wash water use level was materially improved. Similar effects were also found for surfactant 112A where formulations using the "N" silicate were somewhat superior to those with the "Star" grade.

To further follow up the effect of silicate and of pH on the performance of surfactant 212, formulations 212-56 and 212-57 were tested. These formulations completely eliminated the silicate and, in addition, formulation 212-56 was titrated with citric acid to a pH of 7. The silicate free pH of formulation 212-57 was slightly over 9. These two formulations performed surprisingly well being only slightly less effective than their silicate containing counterparts 212-53 and 212-22. Total elimination of silicate also had only a relatively minor negative effect on formulations with surfactant 112A particularly in the fully built formulation 112A-119 and 112A-120. The series 112A-75 to 112A-77 further illustrates this trend. It should be of interest to further investigate this matter and possibly achieve formulations having relatively low pH.

Sodium gluconate also tended to enhance the detergency of formulations using 112A and 212 and combinations of gluconate and acetate were particularly effective. While the acetate and gluconate combinations were very effective with 112A on the UST cloth with relatively little effect on the EMPA cloth (112A-80 and 112A-112), addition of electrolytes improved their efficiency on the EMPA without impairing the effectiveness on the UST cloth (112A-122 to 125). Addition of citrate to these formulations markedly improved the detergency on the EMPA cloth but appeared to diminish their effectiveness on the UST cloth (112A-111, 112A-118 to 121). Surfactant 212 behaved in similar fashion and nearly all of the formulations (212-94 to 96 and 212-128, 130, 131, 134 and 138) ranked among the top ten in the combined cloth rankings.

Seqlene, a proprietary sequestering formulation, the anionic surfactant Gantrez, and Weston, a polyelectrolyte product, were not tested sufficiently to establish any definite trends but appeared to have very little effect on the formulations in which they were investigated.

Surfactant 210, the C_{10} homolog of compound 212, was also tested and found to be somewhat less effective than the C_{12} compound. Although there appeared to be a tendency for the 210 compound to clean slightly better at the 0.5% formulation in the wash water level, these formulations performed consistently worse at the 0.1% and 0.2% use levels than did the corresponding formulations using the C_{12} homolog. The performances of these two homologs are compared in the five formulations (formulations 210-53 to 57) presented in Figures 44-46.

The C_{10} homolog of surfactant 112B1, 110B1 was also investigated. Because of the limited amount of this compound available, it was decided that an abbreviated test method should be used in order to be able to test a larger number of formulations. This approach was preferred since a larger number of formulations would help to establish a definite trend while little could be concluded from the full testing of only one or two formulations. The 110B1 formulations were therefore evaluated only at two concentrations, 0.1% and 0.3% at each of two water hardness levels, 135 and 300 ppm.

The results of this series of tests with the 110B1 compound are presented and compared to those obtained with the 112B1 homolog in Figures 47-49. It will be noted that with all five formulations tested the C_{10} compound outperformed the C_{12} homolog at the higher detergent concentration, while the latter did better at the lower concentrations indicating that the C_{10} detergent efficiency is more affected by concentration factors than its larger homolog. This effect is particularly obvious with the EMPA cloth but less consistent in the UST cloth.

A number of selected formulations using surfactants 112A and 212 were also tested on the dacron/cotton wash-and-wear fabrics. Both of these compounds performed well on both the permapress finished cloth as well as the cloth without this finish. Most of the formulations with 212 easily outperformed the two reference standards while those with 112A, although not quite as consistently effective did well at the lower concentrations in the higher hardness water. Both types of cloth, as supplied by Testfabrics, come with only half their width soiled leaving a white flag which permits the simultaneous testing for redeposition. We washed these cloths, therefore, with the flags attached to determine whiteness retention. In none of the formulations tested did we find any significant loss of whiteness. The detergency data for the dacron/cotton cloths are presented in Figures 50-55 and the whiteness retention values are given in Tables 12-13.

The consistent failure of surfactant 112B1 to perform as well as the other two compounds clearly eliminated it from consideration in our final recommendations, although we believe that it has sufficient promise to warrant further investigation.

Although some of the formulations using surfactant 212 appear to be superior to any of the 112A formulations, we have some reservations about recommending these at this time. It was our practice to use the 212 in the form of a slurry as obtained in a single step extraction from the reaction mixture. This slurry usually contained about 30% active surfactant, the balance being a 1:1 mixture of isopropanol and water. A recent test using dried surfactant 212 yielded detergency results approximately 15% lower than those obtained with the identical formulation using the slurry. This may indicate that some detergency effects were contributed by the isopropanol. Since, in a finished, spray-dried detergent product these effects would also be absent, we hesitate to choose this surfactant without further investigation into this problem. We strongly

Table 12

WHITENESS RETENTION[a]
Decron/Cotton (65/35) Fabric With and Without Permapress Finish[b]
112A Formulations

Sample No.	50 ppm								135 ppm								300 ppm							
	Without				With				Without				With				Without				With			
	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5
H	0.7	0.8	0.8	0.4	0.6	0.9	0.6	0	1.1	0.8	1.2	1.4	2.7	2.9	3.0	2.6	0.7	1.0	1.3	1.3	0.6	1.0	1.2	1.0
J	-2.2	-0.3	-0	-0	-2.5	-0.9	-0.2	0.5	0.4	-0.9	-0.2	0.6	0.7	-0.6	-0.5	-0	1.0	1.1	0.8	0.9	0.5	0.6	0.5	-0
72	0.6	0.1	-0.3	-0.2	1.4	-0	-0.8	-0.8	0.9	0.4	0.7	0.7	-0.2	0.4	0.3	0.6	1.0	1.9	1.2	0.9	0.4	0.6	0.3	0.6
75	-1.1	0.1	0.4	0.7	-2.2	-0.3	1.6	2.2	0.2	0.4	0.7	0.9	1.7	2.0	1.8	2.0	0.3	1.6	1.7	1.3	2.9	2.3	2.1	2.0
77	-1.4	0.2	0.4	0.8	-4.1	-1.0	-1.0	-0.1	-1.9	-0.2	-0.1	0.4	-4.3	-1.8	-1.1	-0.8	0.8	0.6	0.2	0.2	-0.4	-0.5	-0.9	-0.6
78	-3.3	-2.1	-0.7	-1.1	-3.5	-1.8	-1.8	-0.7	-0.3	-1.0	0.1	0.3	-0.4	-1.2	-0.7	-0.4	0.8	0.8	0.6	0.5	0.4	0.5	0.1	-0.4
80	1.7	2.1	2.1	2.3	2.0	2.2	3.2	2.8	2.4	2.6	1.4	1.8	1.3	1.8	2.0	1.8	1.8	1.9	1.6	1.8	1.2	1.8	2.3	2.1
104	-0.8	0.7	1.0	1.0	-1.7	1.5	0.1	0.4	0.7	0.8	1.0	0.9	-0.2	-0.5	-0.1	0.4	1.1	0.9	1.0	1.0	0.2	0.4	0.6	0.7
117	0.8	1.2	0.8	0.4	1.5	2.3	2.4	2.2	1.1	1.5	1.5	1.4	2.1	2.3	2.3	3.1	1.1	0.9	1.3	1.7	1.9	2.0	2.3	2.7
118	-2.3	-0.4	0.4	0.5	-3.5	-1.7	-1.2	-0.2	-1.0	-0.1	0.3	0.9	-2.8	-2.0	-1.5	-0.8	0.3	1.5	0.9	1.0	-0.1	-0	-0.5	-0.2
121	-1.9	-1.4	0.6	1.0	-4.1	-1.7	-1.0	-0.7	0.9	0.8	0.5	0.8	-0.5	-0.8	-0.6	-0.6	1.1	1.1	1.0	0.5	-0.3	-0	-0.2	-0.4
125	-3.1	-0.6	0.1	1.2	-2.9	-1.6	-1.3	-0.7	0.8	1.0	1.1	0.7	-0.6	-0.2	-0.5	-0.8	0.8	1.2	1.3	1.4	-0.4	-0.3	-0.2	-0.1
Brand	1.3	1.1	1.7	1.7	1.5	2.0	1.9	2.6	0.5	1.2	1.4	1.5	1.3	1.8	2.0	2.2	0.4	1.0	1.5	1.9	2.0	1.9	2.0	2.5
AHAM	-1.8	-1.0	-0.8	0.5	-0.3	0.6	0.7	1.5	-3.5	-0.5	-0.5	0.9	-2.0	-0.2	0.4	1.7	-1.9	-3.0	-0.8	-0.3	-1.0	0.4	0.7	0.5

[a] Differences in reflectivity; negative values mean loss in reflectivity after washing.

[b] Standard soiled cloth with attached white flag from Testfabrics, Inc.

Table 13

WHITENESS RETENTION[a]
Dacron/Cotton (65-35) Fabric With and Without Permapress Finish[b]
212 Formulations

Sample No.	50 ppm								135 ppm								300 ppm							
	Without				With				Without				With				Without				With			
	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5
30	-1.7	-0.5	-0.1	-0	-1.5	-1.1	-0.8	-0.5	0.8	0.4	1.0	0.4	0.2	0.1	-0.3	-0.5	1.1	1.2	1.1	0.9	-0.6	0.5	0.2	-0
43	0	0.5	0.8	1.2	-0.3	-0.6	-0.1	0.4	0.2	0	0.5	1.2	-0.3	-0.5	-0.4	0.4	0.4	0.1	-0	0.6	-0.2	-0	-0.4	0.2
44	0.4	0.3	1.7	0.6	-0.4	-0.5	-0.8	-0.6	0.9	1.2	1.1	0.8	0.2	0.4	0.2	0.1	0.7	0.6	1.3	1.1	-0.3	0.6	0.6	0.3
74	0.1	0.8	1.0	1.0	-1.0	-0.5	-0	0.4	0.5	0.7	0.8	1.0	-0.5	-0.1	-0.1	0.6	0.4	0.5	0.6	1.2	-0	0.4	0.3	0.7
89	-1.0	0.2	0.5	0.9	-1.9	-0.3	-0.6	-0	0.6	0.2	0.5	0.6	-0.4	-0.3	-0.5	-0.1	0.9	0.9	1.1	0.8	-0	-0.4	-0	-0.1
130	-0.8	0.3	0.6	0.9	-1.6	-0.7	-0.8	-0.3	0.8	0.5	0.8	1.0	-0	-0.6	-0.4	-0.4	1.1	1.2	1.0	1.0	0.3	0.5	0	0
132	-0.4	-0.4	0.7	1.1	-2.0	-1.4	-1.4	-0.6	0	0.5	0.5	1.0	-3.0	-1.1	-0.9	-0	0.9	1.1	1.0	0.8	-0.2	-0.2	-0.6	-0.6
136	-0.4	-0.3	0.6	1.1	-2.9	-1.1	-1.1	-0.6	0.4	0.2	0.8	1.0	-1.3	-1.1	-0.8	-0.3	1.0	1.1	0.8	1.0	-0.3	0.1	0.4	-0.4
Brand	0.3	0.8	0.8	1.4	-0.6	0.2	0.1	0.8	0.1	0.5	0.8	1.3	-0.2	-0.1	0.2	0.7	1.1	0.8	0.2	1.0	0.4	0.3	0.3	0.5
AHAM	-1.8	-1.0	-0.8	0.5	-0.3	0.6	0.7	1.5	-3.5	-0.5	-0.5	0.9	-2.0	-0.2	0.4	1.7	-1.9	-3.0	-0.8	-0.3	-1.0	0.4	0.7	0.5

[a] Differences in reflectivity; negative values mean loss in reflectivity after washing.

[b] Standard soiled cloth with attached white flag from Testfabrics, Inc.

recommend the further investigation of this surfactant, however, since even at these lowered detergency levels some of the formulations would still compare favorably with formulations using 112A.

The final choice of the formulation which we are recommending for full-scale consumer use and ecological compatibility testing (112A-121) depended on the consideration of several factors. While not the best formulation tested, its choice was a compromise based on its relatively good performance at the low concentration and in the medium hard water which is close to the water hardness most commonly found in the U. S. Although it ranks rather low on UST cloth (26 out of 63) a glance at the actual detergency data shows that its performance is, in fact, quite close to that of the best. This problem of low rank values for relatively well performing formulations was discussed earlier and is particularly critical here since for some of the test conditions nearly half of the 112A formulations yielded detergency data falling within a range of only 5 RU. With such a narrow range, differences in the actual performance of the individual formulations are relatively insignificant but become blown up out of proportion by being spread over a much larger range of rank numbers. Thus, in spite of its low rank, formulation 112A-121 performs very well on UST cloth. This is further borne out by the fact that in the combined cloth ranking this formulation scored 51 out of a possible 59, indicating that its overall performance was, in fact, good.

The composition of the formulation appears to be quite innocuous in the sense that all builders used are present in relatively low concentrations and none of them are likely to affect the ecology adversely. Although the pH of this formulation (approx. 10) is somewhat higher than we would like, it is commensurate with that of most common phosphated brands. None of the components should pose any hazard to safety. Finally, it is a 100% solids formulation, thus requiring no further formulation effort.

Economical factors were not considered in the production of any of our formulations, nor were these within the intent of this program. Since none of the candidate surfactants are currently being commercially manufactured their eventual price will depend largely on the degree of acceptance these surfactants command. This also applies to the cost of some of the formulation constituents, like sodium citrate, whose price will depend largely upon the demand created for them.

SECTION VII

ACKNOWLEDGMENTS

This project was carried out by the IIT Research Institute under Contract No. 14-12-937 for the U. S. Environmental Protection Agency.

The concept of using potentially "self-chelating" surfactants in phosphate free detergent formulations was fostered by Dr. Warner M. Linfield, formerly Manager, Organic Chemistry Research Section, IITRI. Additional formulation ideas were contributed by Mr. Helmut G. Reilich, Associate Chemist.

IITRI personnel who directly participated in this project include L. Hytry, F. Ribich, L. Ward, C. Wetter and T. Yamauchi of the Organic Chemistry Research Section. The fish Toxicity and the Provisional Algael Assay Procedures were carried out by Biometrics Laboratories, Englewood Cliffs, New York under the direction of Dr. Samuel Posner.

Special thanks are given to Dr. C. C. Harlin, Jr., Chief of the Water Quality Control Research Program, Robert S. Kerr Water Research Center, EPA, whose suggestions and interest provided guidance in the evaluation of our work.

This project was designed, operated and administered by IITRI; Dr. Warner M. Linfield was Project Director and Mr. Helmut G. Reilich was Project Leader.

SECTION VIII

REFERENCES

1. "Development of Phosphate-Free Home Laundry Detergents," Water Pollution Control Research Series No. 16080DVF 12/70, EPA, U. S. Government Printing Office, Washington, D. C.

2. Osaka Shiritsu Daigaku Kaseigakunu-Kiyo, 12, 29 (1964); CA, 63:13582b.

3. H. Schott, J. Am. Oil Chemists' Soc., 45, 414 (1968).

4. R. C. Davis, Soap & Chem. Specialties, 39(8), 47 (1963).

5. A. M. Schwartz and J. Berch, Soap & Chem. Specialties, 39(5), 78 (1963).

Preceding page blank

SECTION IX

APPENDIX A

Additional data for detergency and ranking

Figures 8-13 - Detailed Detergency Performance Data for Compound 112A Formulations on UST and EMPA Cloth

Figures 14-19 - Detailed Detergency Performance Data for Compound 112B1 Formulations on UST and EMPA Cloth

Figures 20-25 - Detailed Detergency Performance Data for Compound 212 Formulations on UST and EMPA Cloth

Figures 26-31 - Performance of Compound 112A Formulations at 0.1% Concentration in Wash Water

Figures 32-37 - Performance of Compound 112B1 Formulations at 0.1% Concentration in Wash Water

Figures 38-43 - Performance of Compound 212 Formulations at 0.1% Concentration in Wash Water

Figures 44-46 - Comparison of Performance of Compound 212 and 210

Figures 47-49 - Comparison of Performance of Compounds 112B1 and 110B1

Figures 50-52 - Performance of Compound 112A Formulations on Dacron/Cotton Fabrics

Figures 53-55 - Performance of Compound 212 Formulations on Dacron/Cotton Fabrics

Preceding page blank

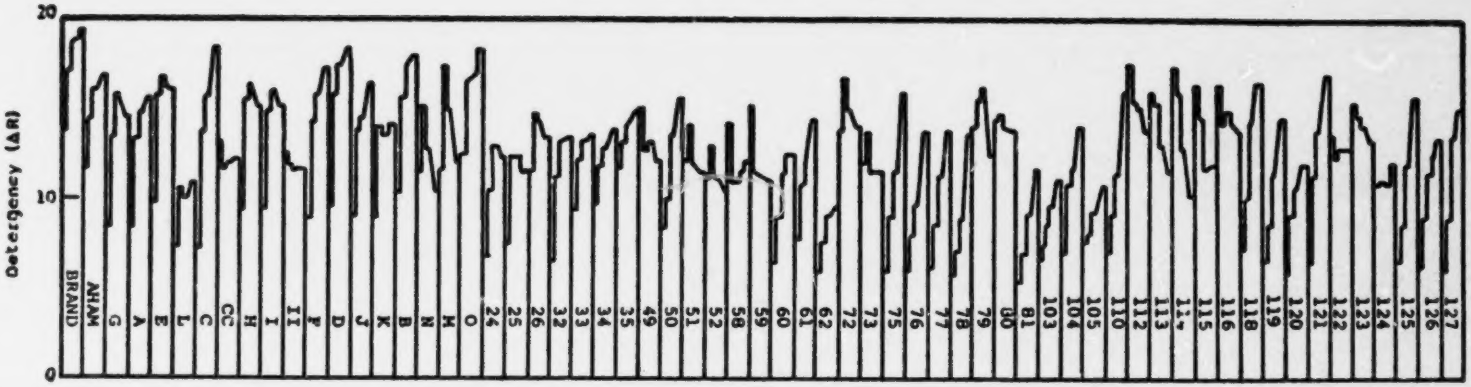


Figure 8

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON UST CLOTH
50 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

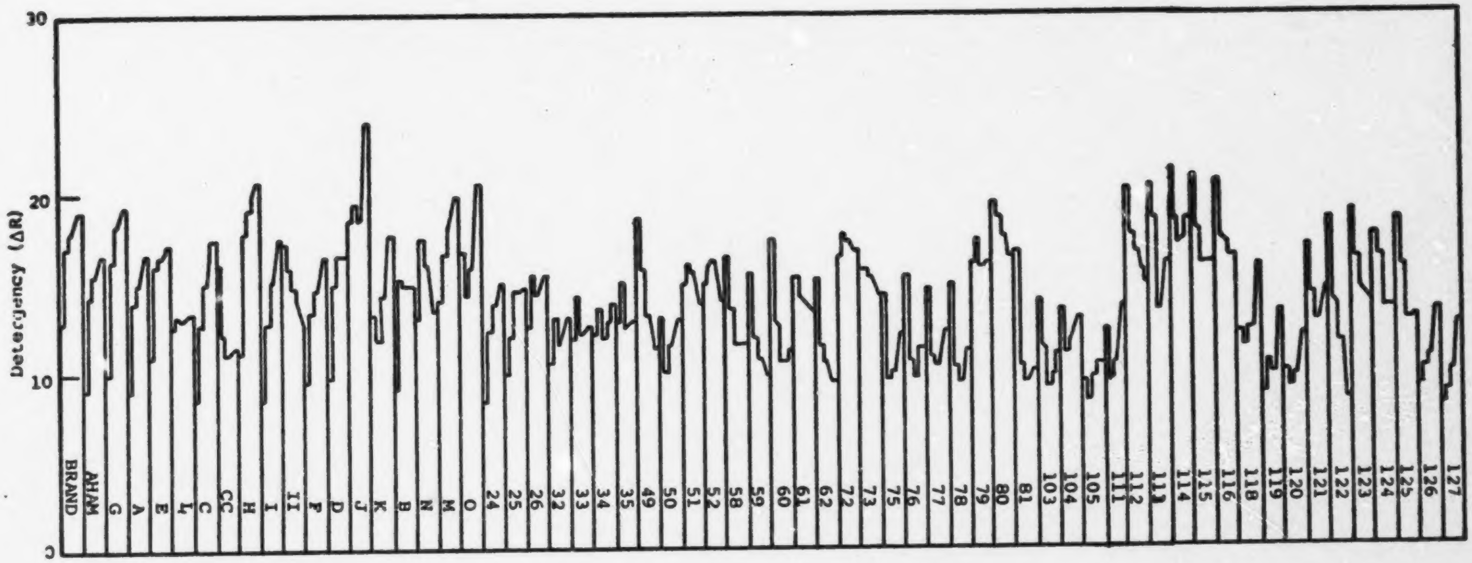


Figure 9

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON UST CLOTH
135 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

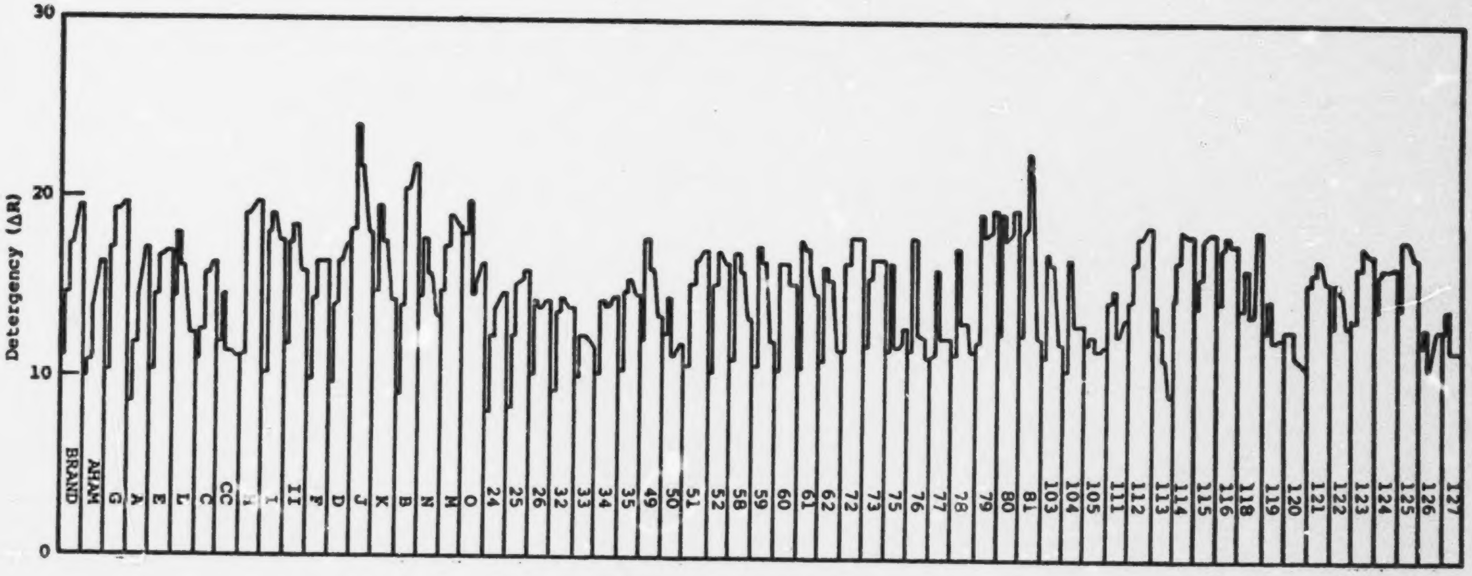


Figure 10

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON UST CLOTH
300 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

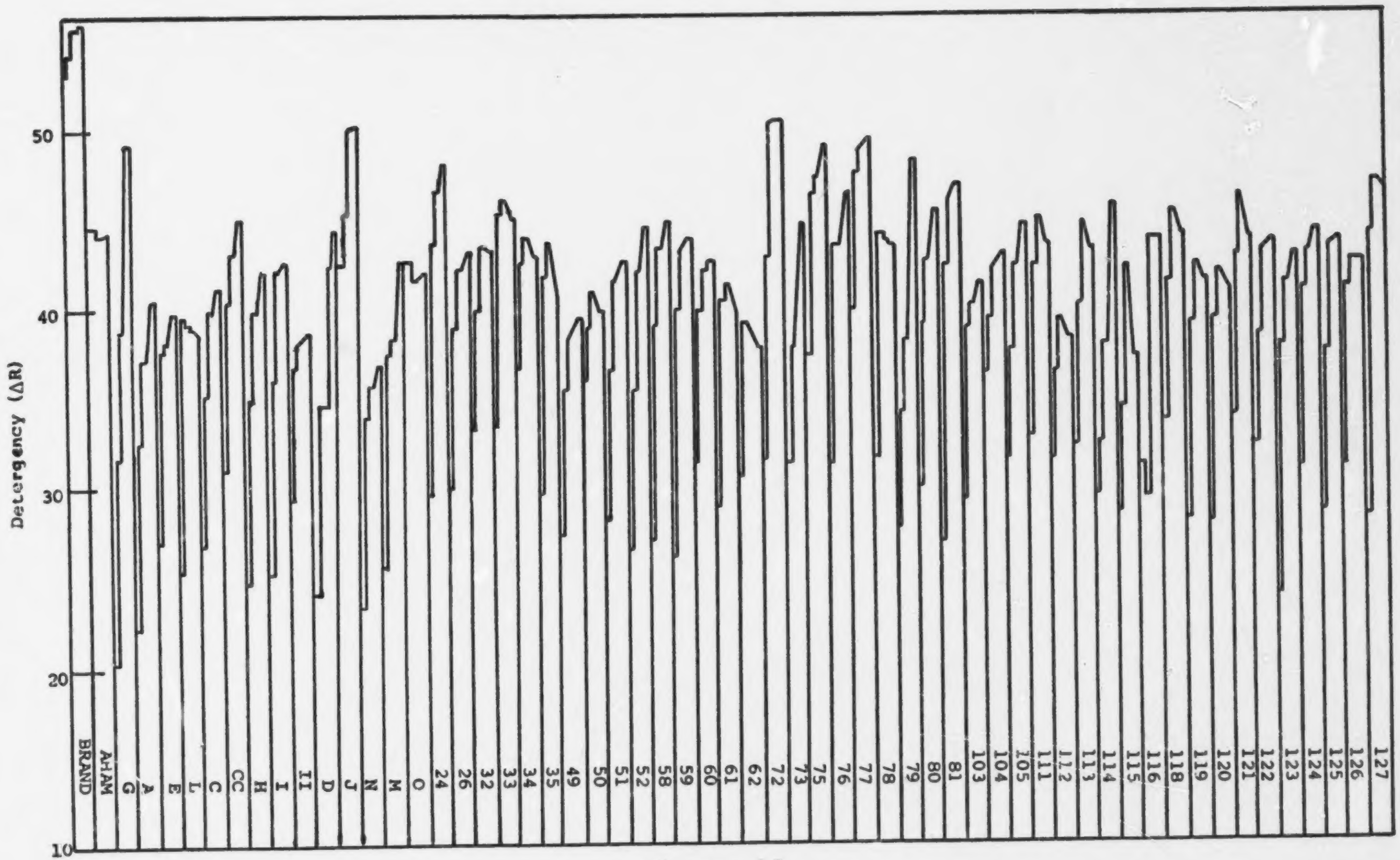


Figure 11

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON EMPA CLOTH
50 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash water

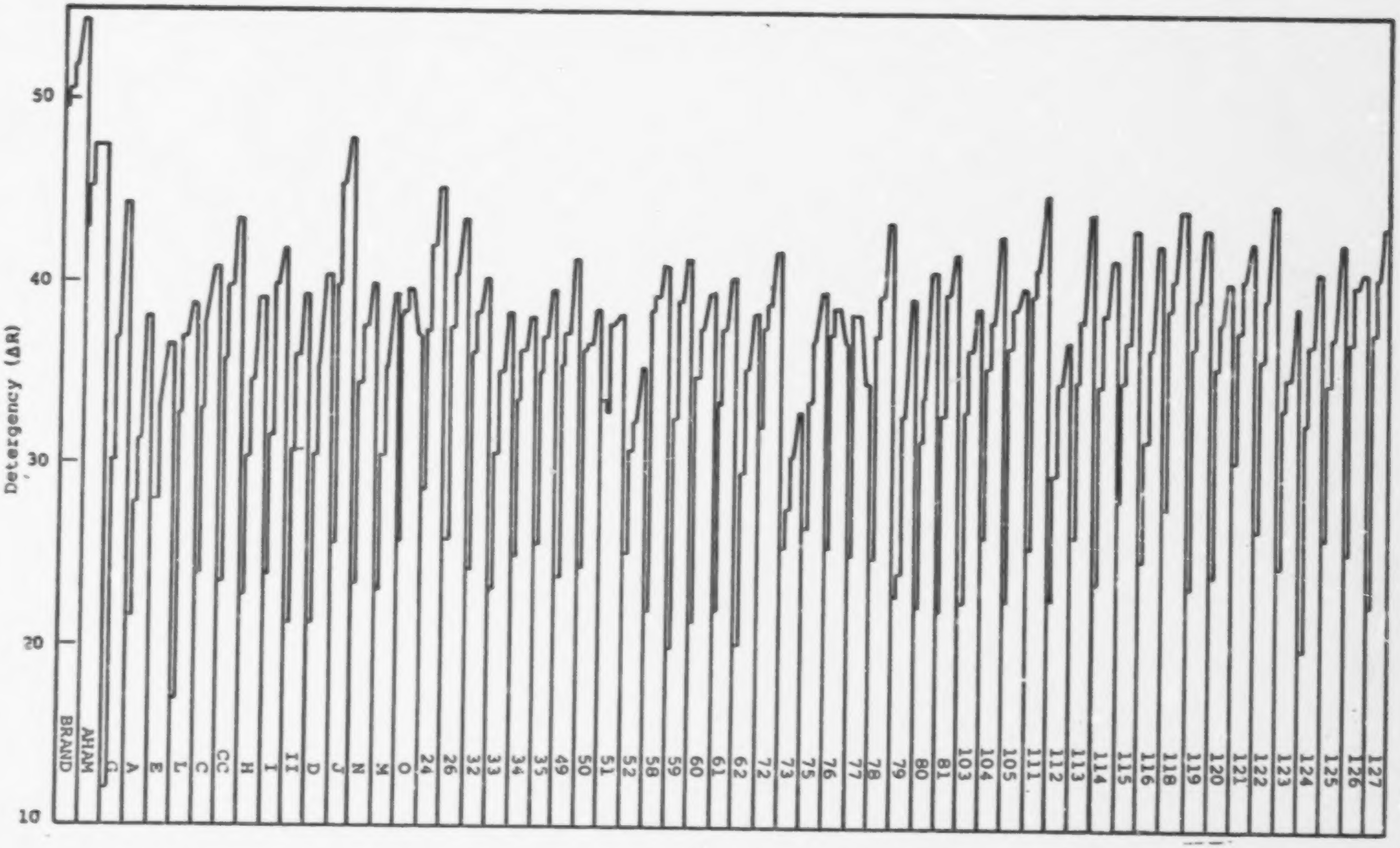


Figure 12

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON EMPA CLOTH
135 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

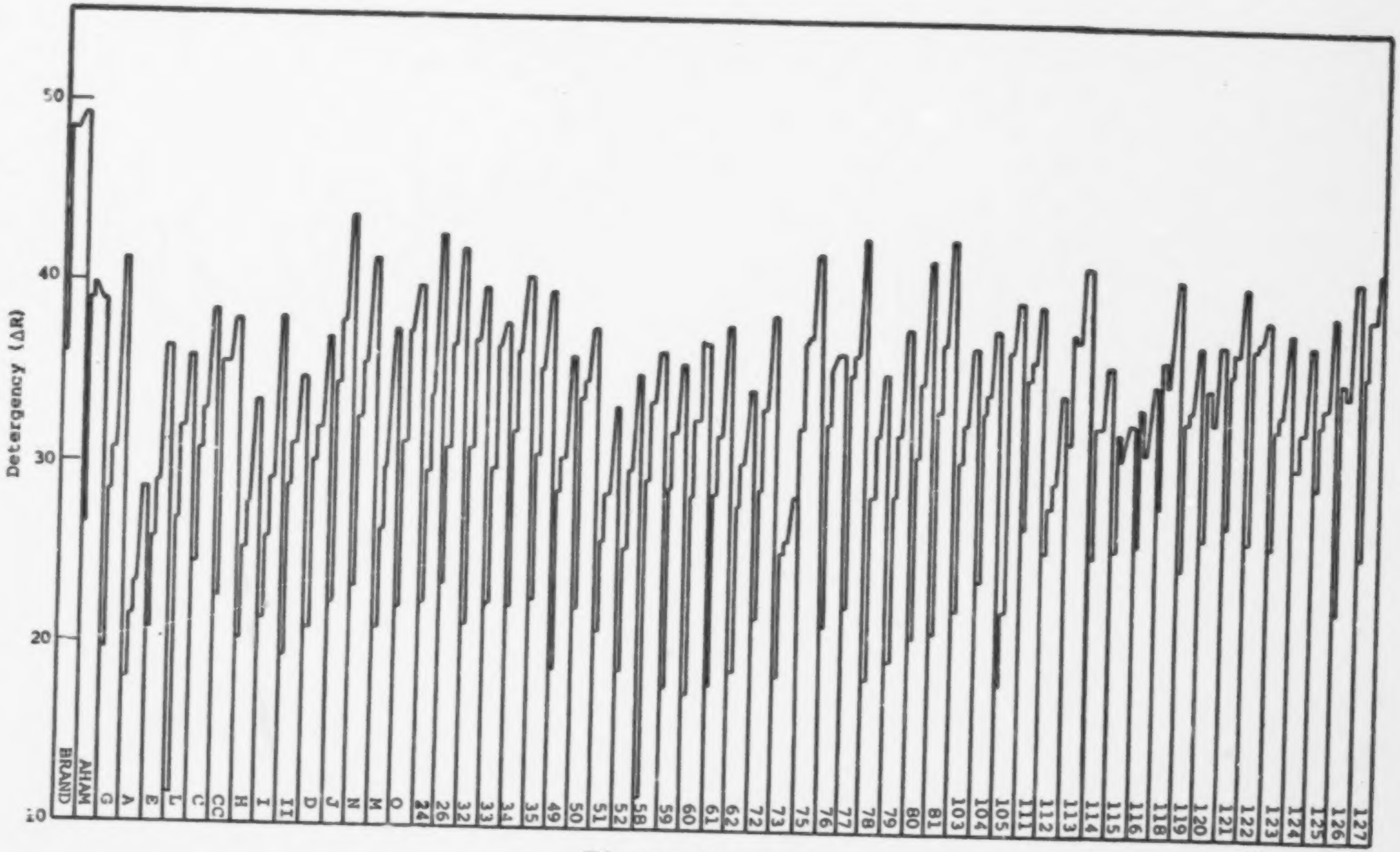


Figure 13

PERFORMANCE OF COMPOUND 112A FORMULATIONS ON EMPA CLOTH
300 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5% Formulation in Wash Water

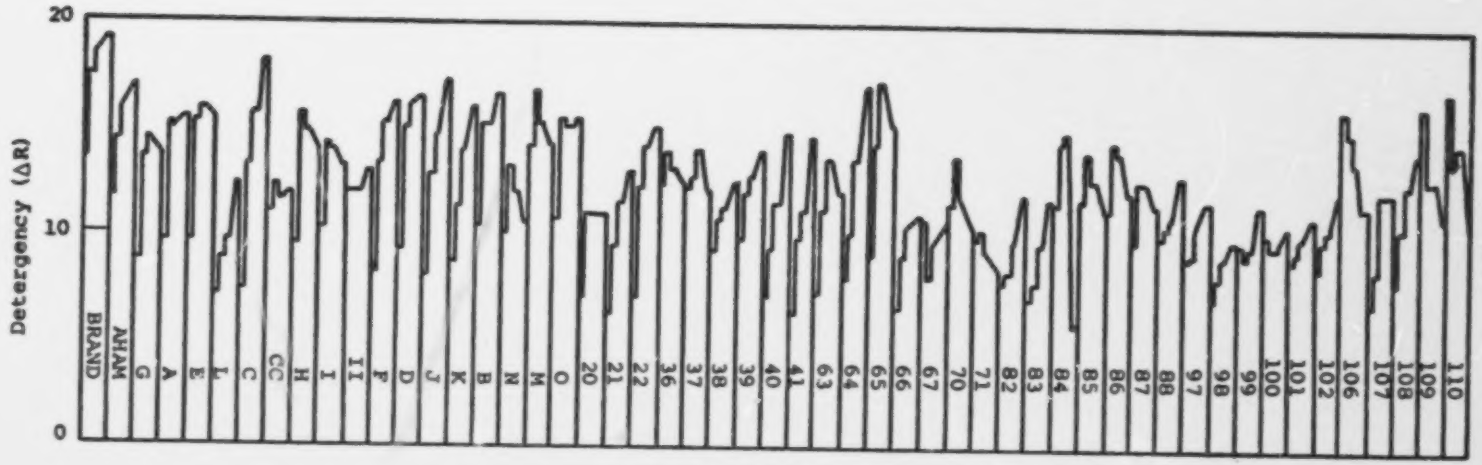


Figure 14

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON UST CLOTH
50 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

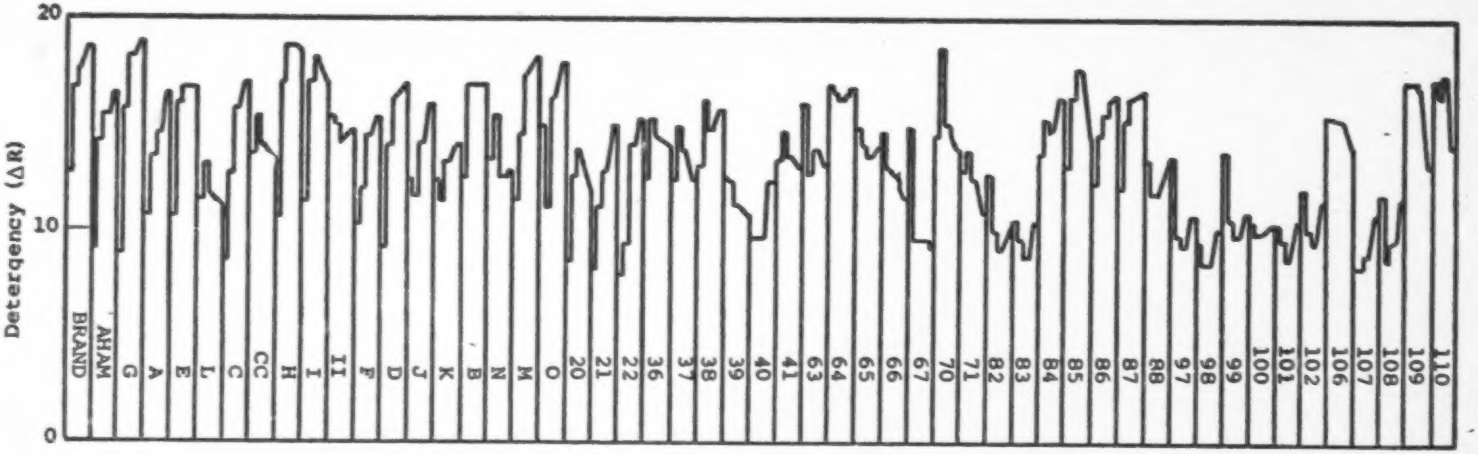


Figure 15

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON UST CLOTH
135 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

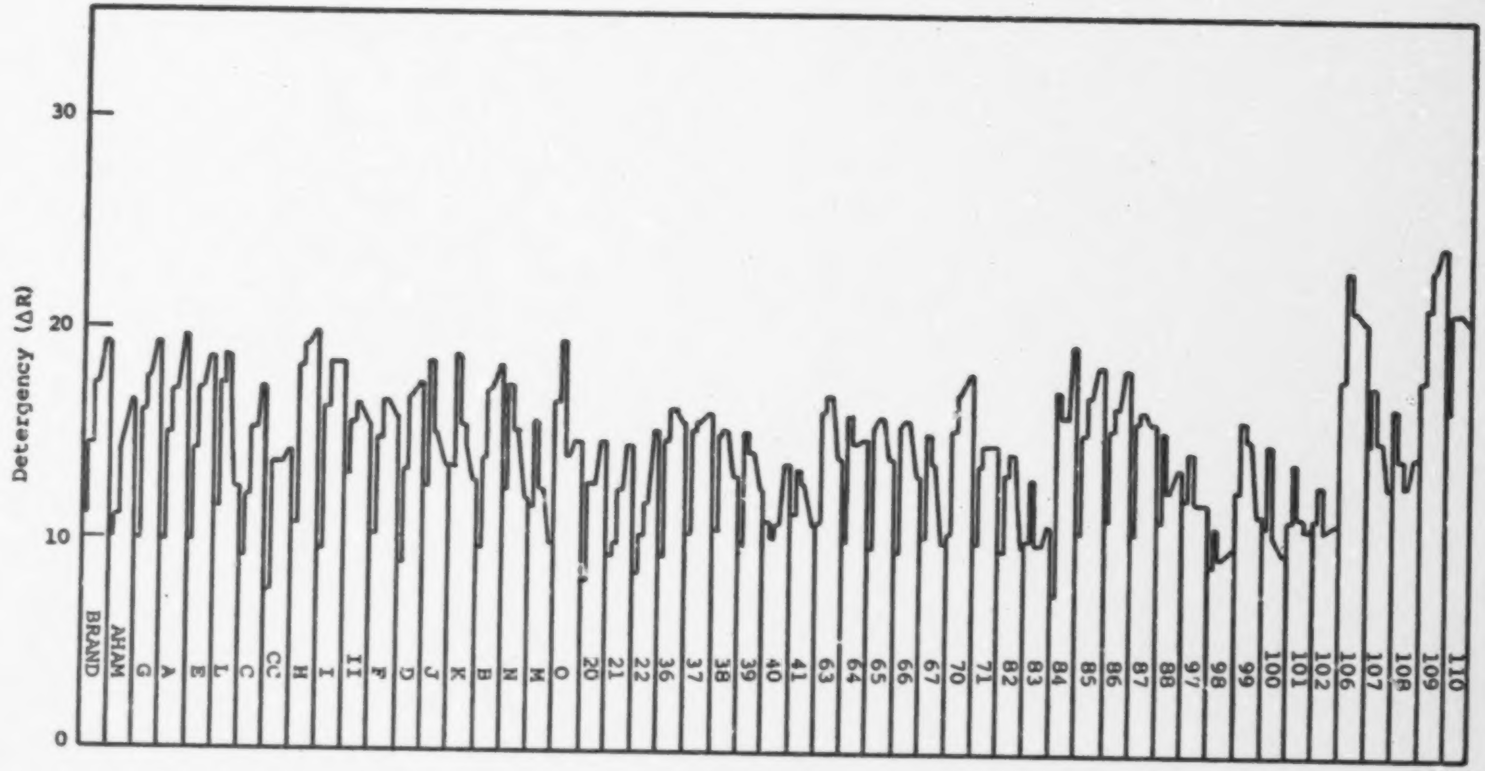


Figure 16

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON UST CLOTH
300 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

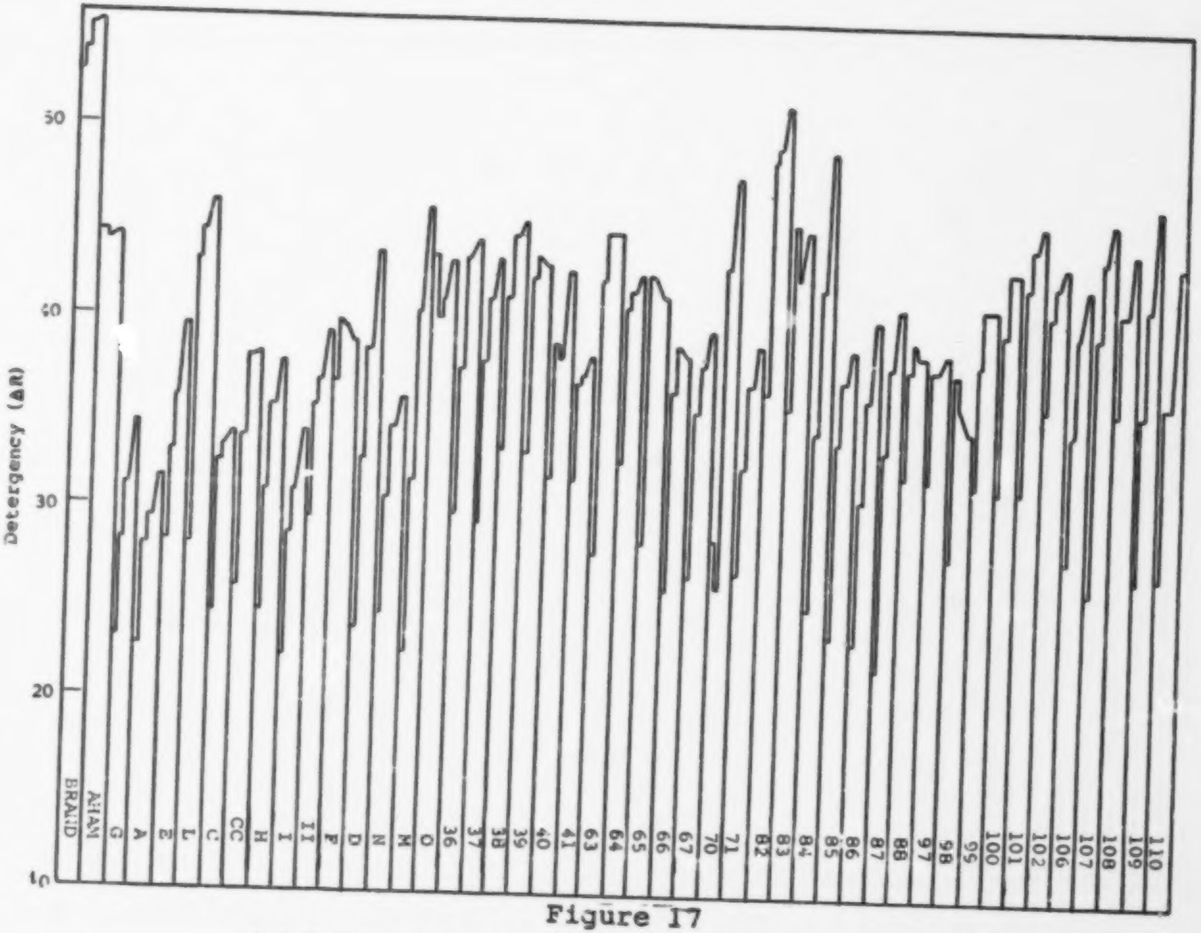


Figure 17

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS ON EMPA CLOTH

50 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5% Formulation in Wash Water

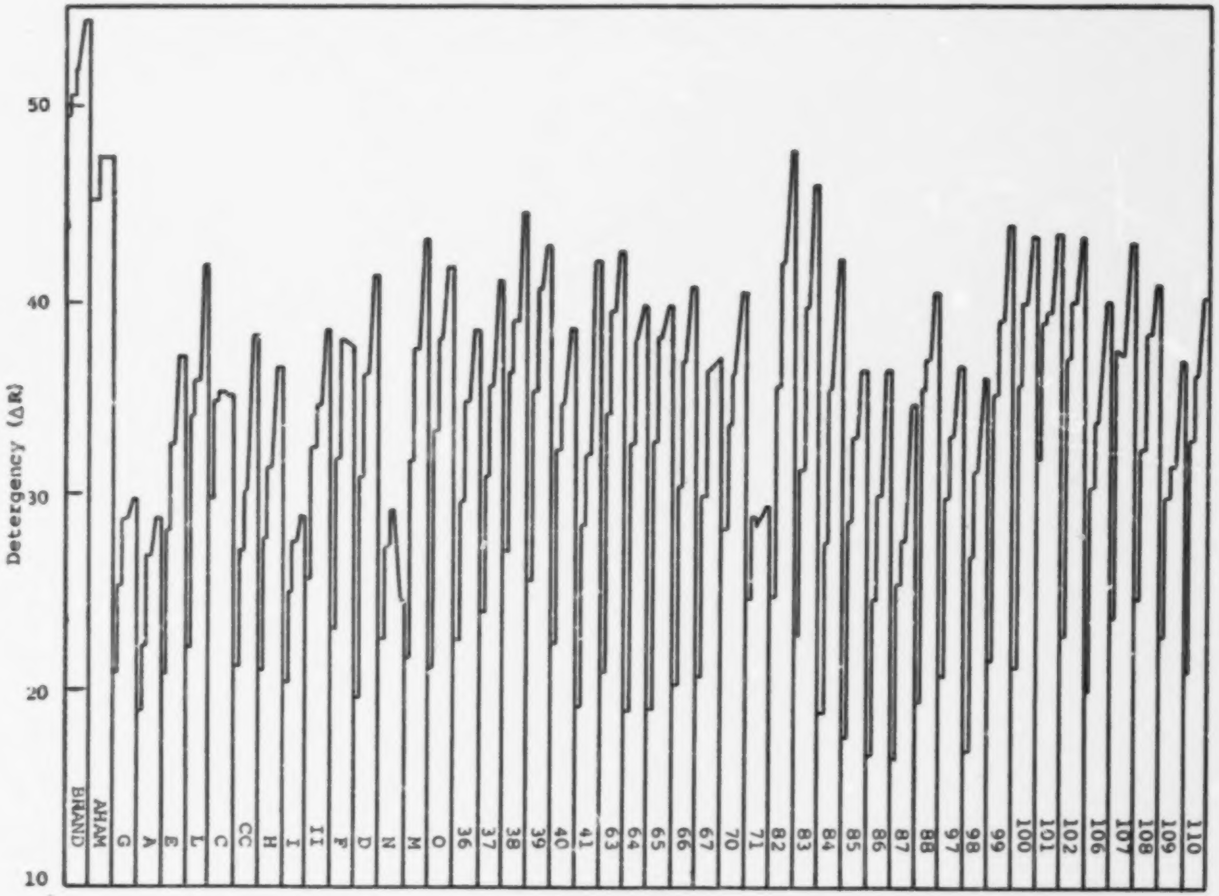


Figure 18

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS ON EMPA CLOTH
135 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5% Formulation in Wash Water

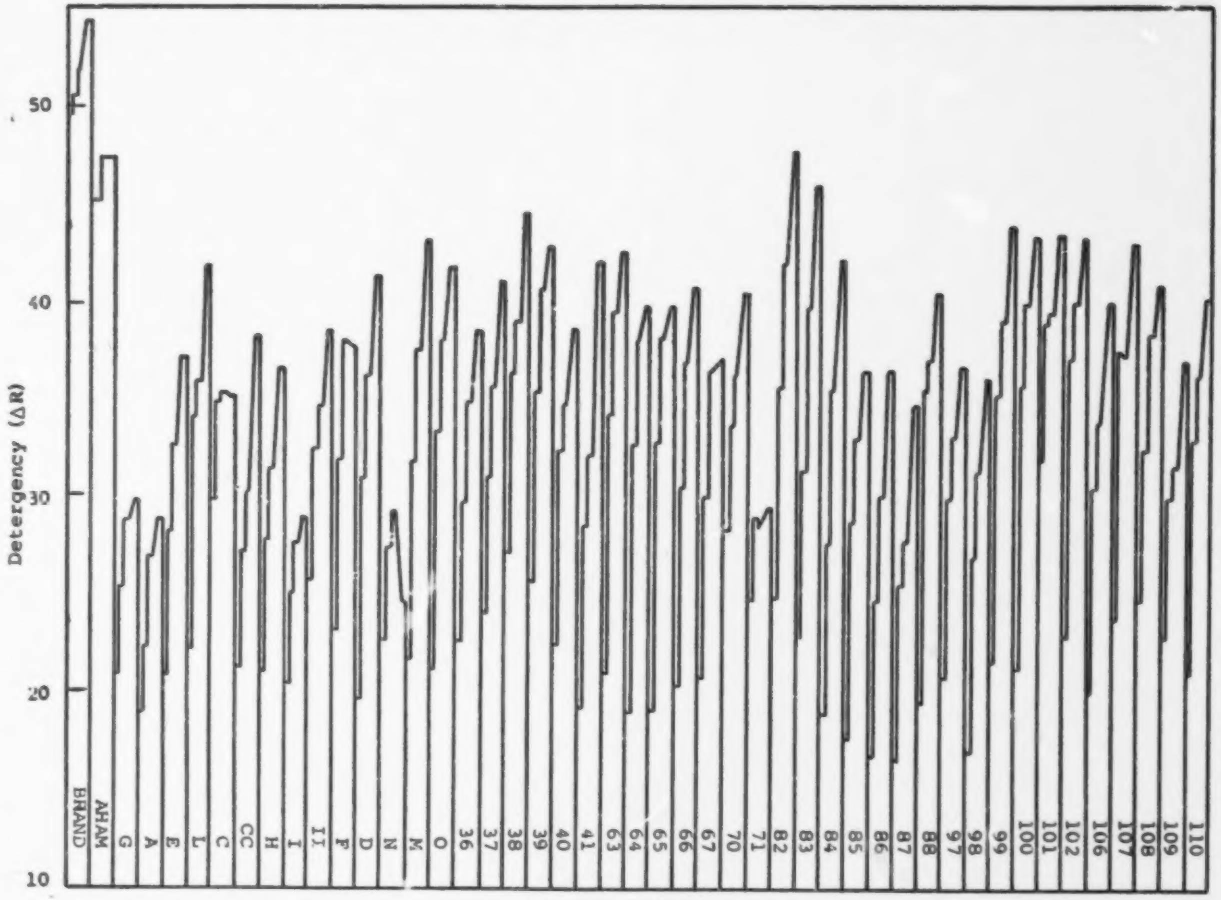


Figure 18

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS ON EMPA CLOTH

135 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5% Formulation in Wash Water

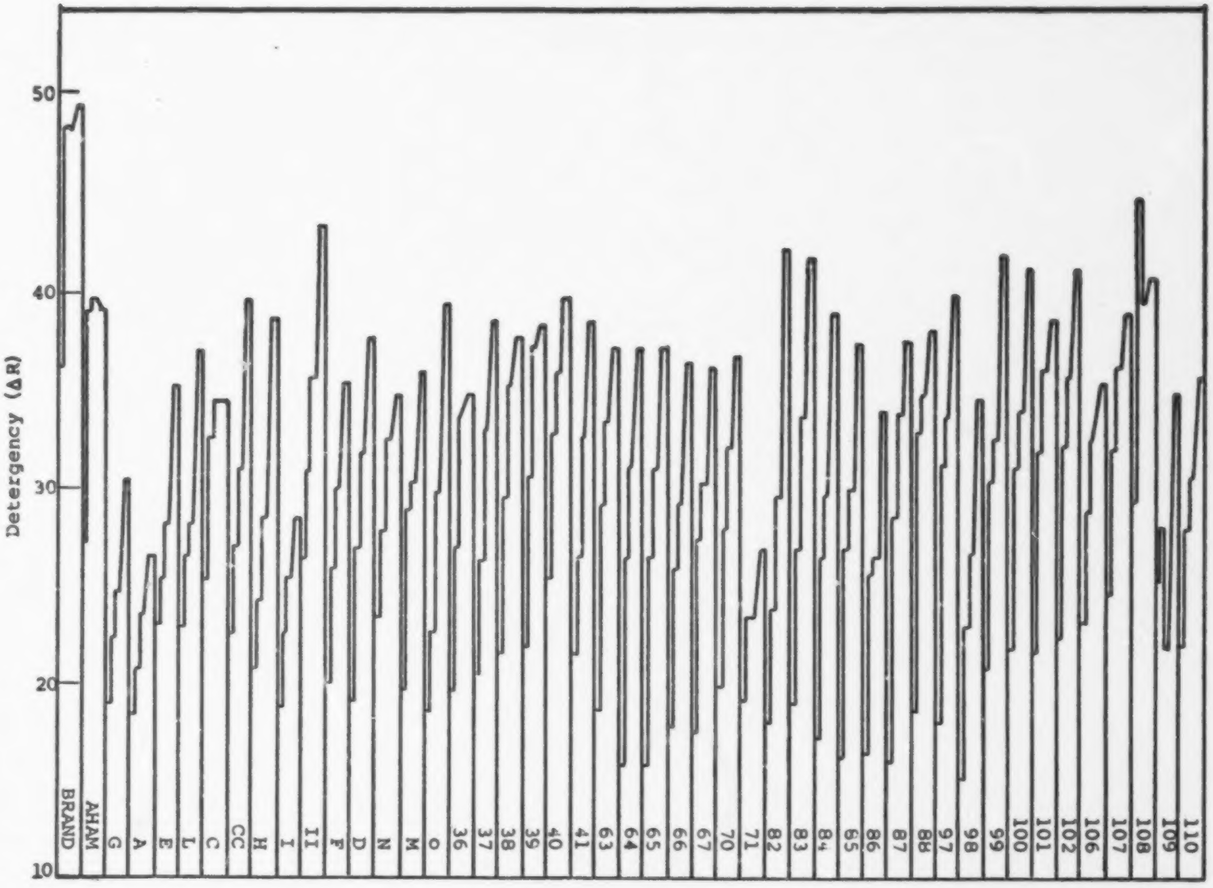


Figure 19

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON EMPA CLOTH
300 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

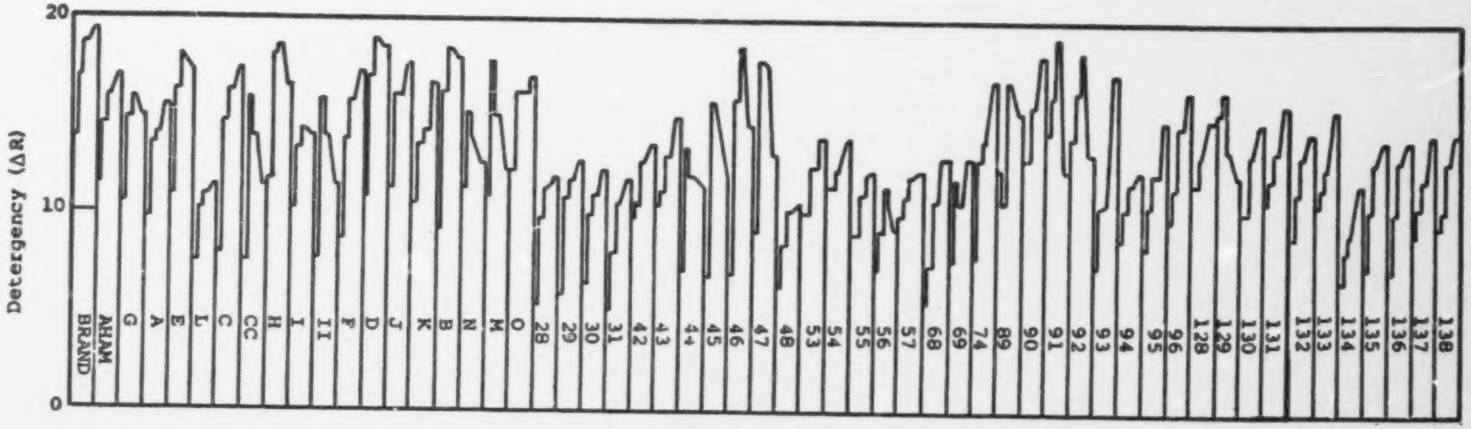


Figure 20

PERFORMANCE OF COMPOUND 212 FORMULATIONS ON UST CLOTH
50 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5% Formulation in Wash Water

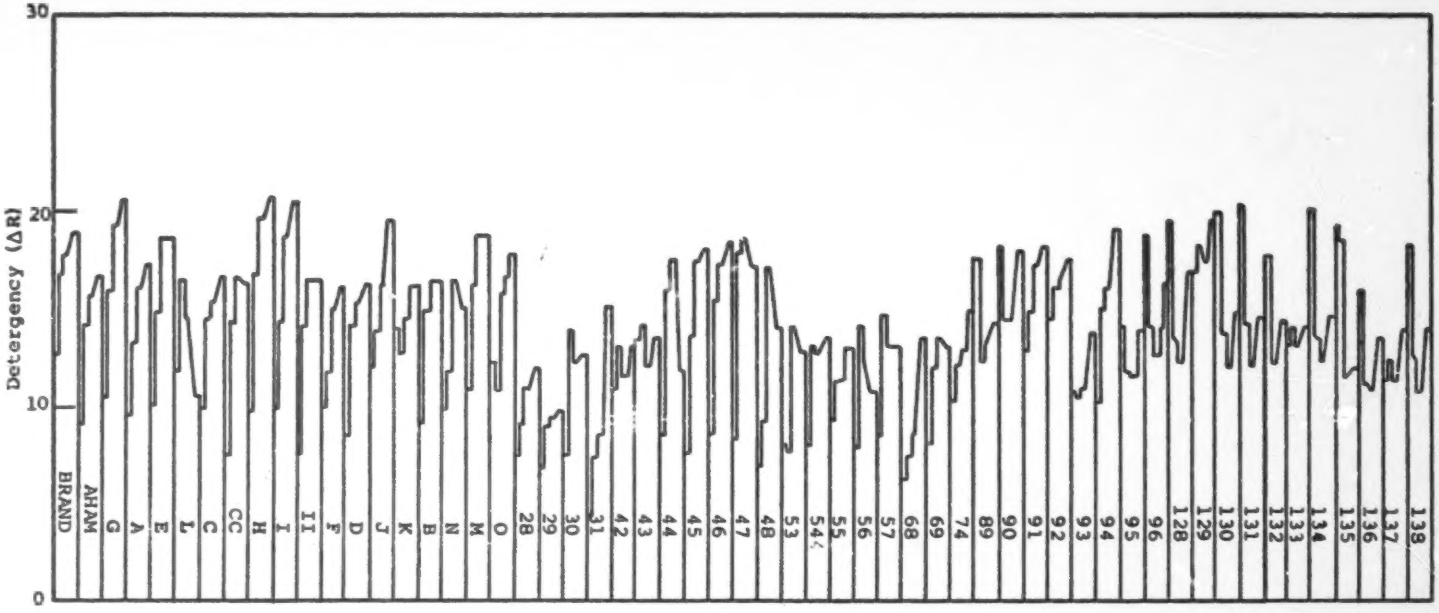


Figure 21

PERFORMANCE OF COMPOUND 212 FORMULATIONS ON UST CLOTH
135 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5% Formulation in Wash Water

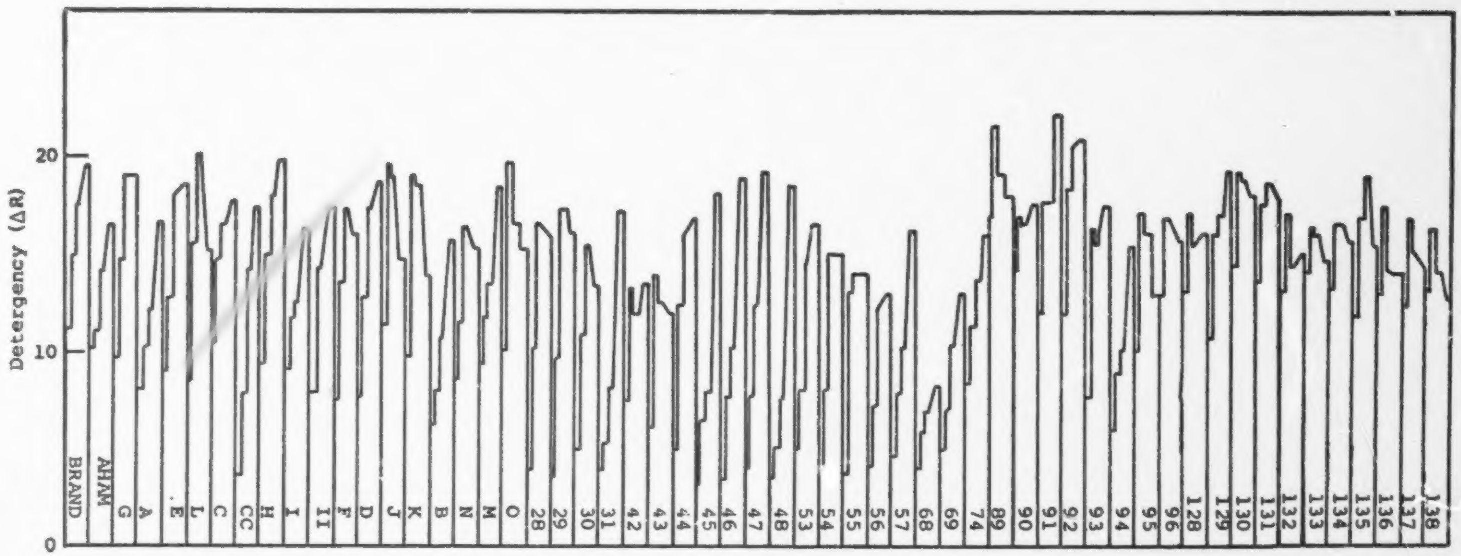


Figure 22

PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON UST CLOTH
300 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

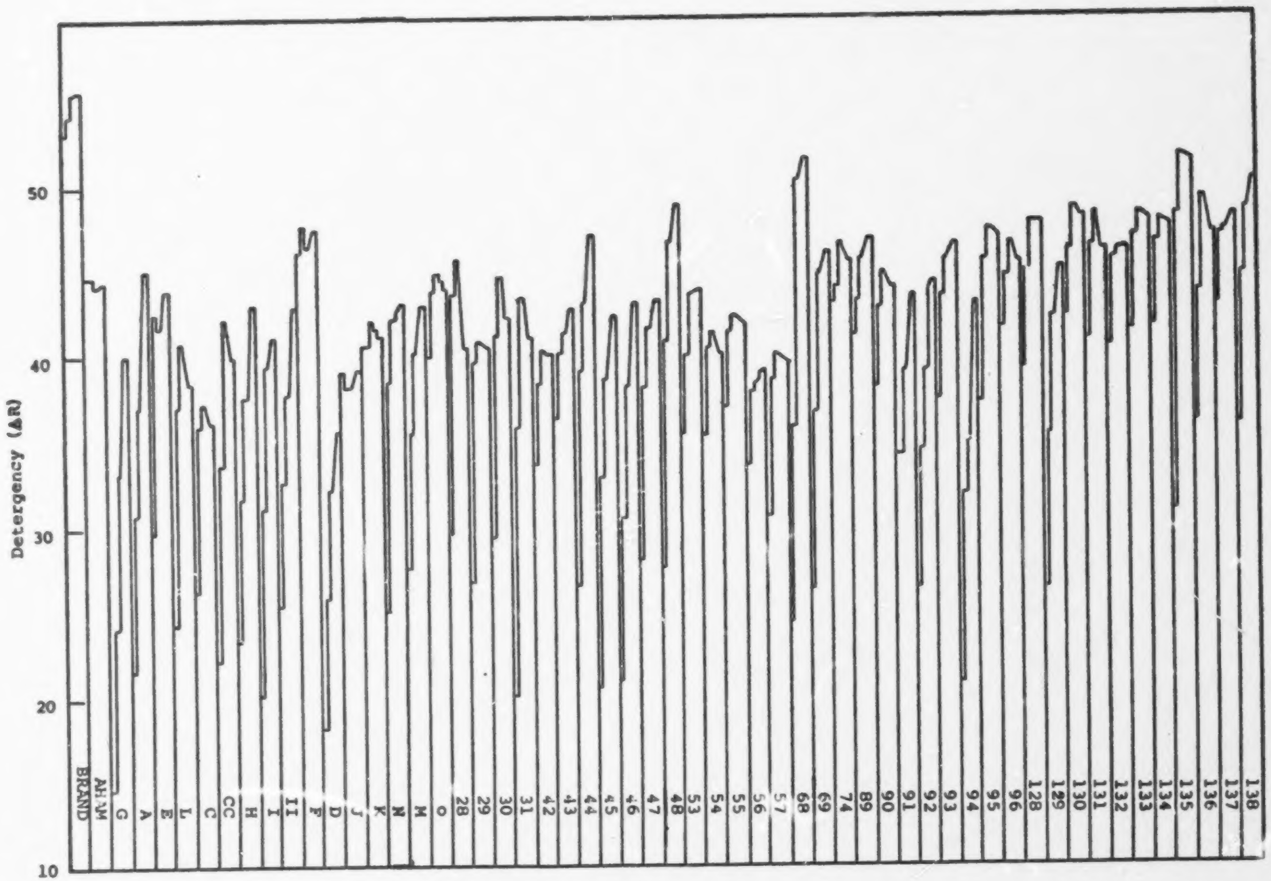


Figure 23

PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON EMPA CLOTH
50 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

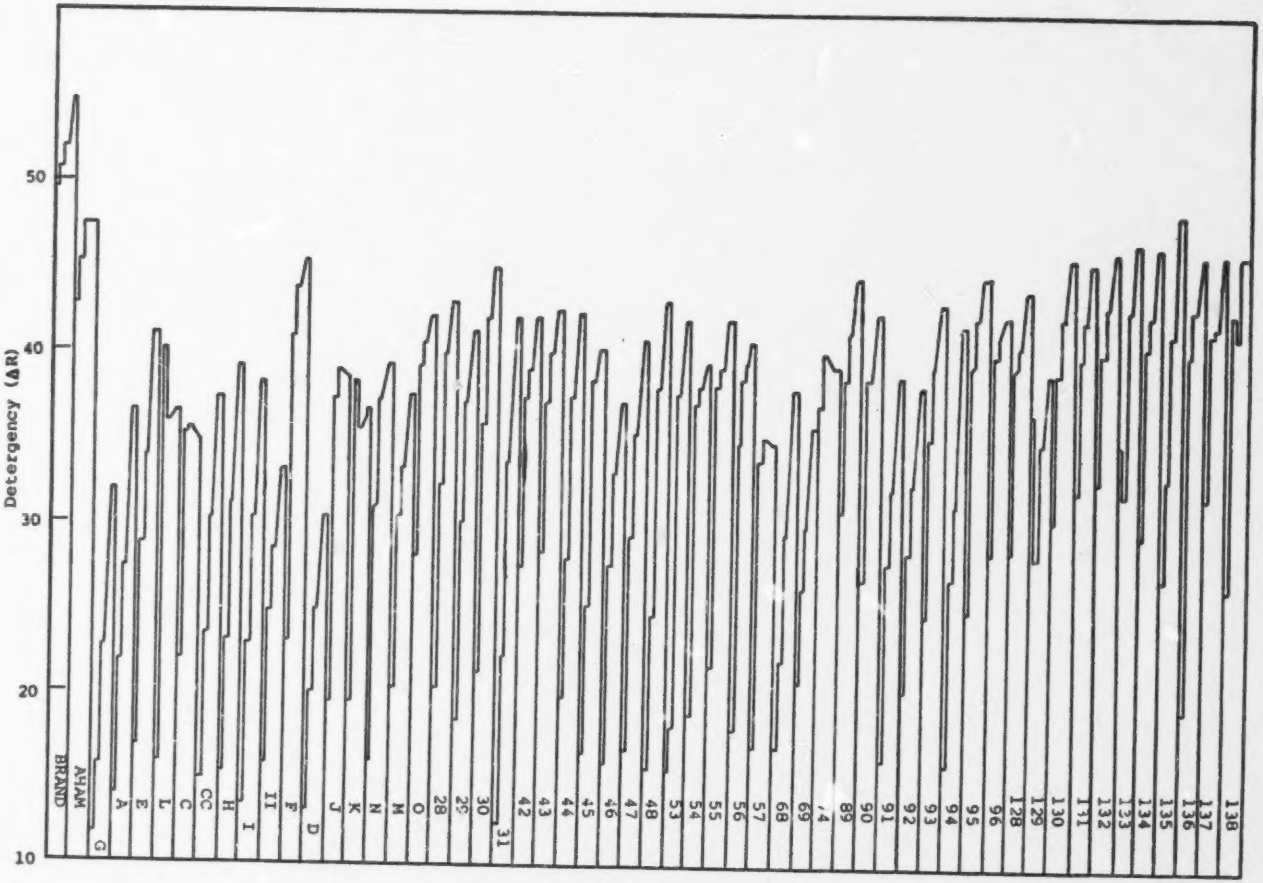


Figure 24

PERFORMANCE OF COMPOUND 212 FORMULATIONS ON EMPA CLOTH
135 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5% Formulation in Wash Water

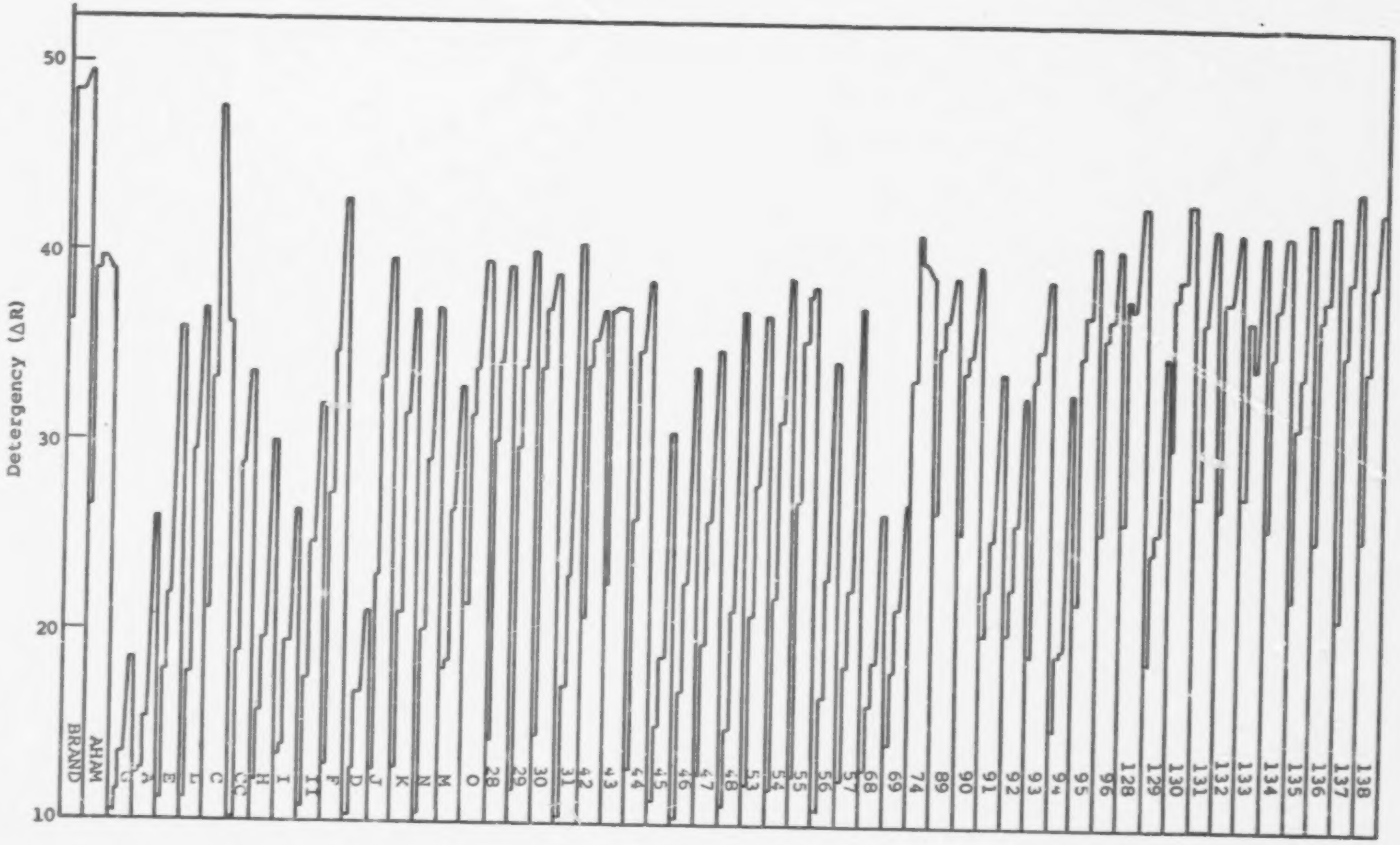


Figure 25

PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON EMPA CLOTH
300 ppm Water Hardness - 0.1, 0.2, 0.3 and 0.5%
Formulation in Wash Water

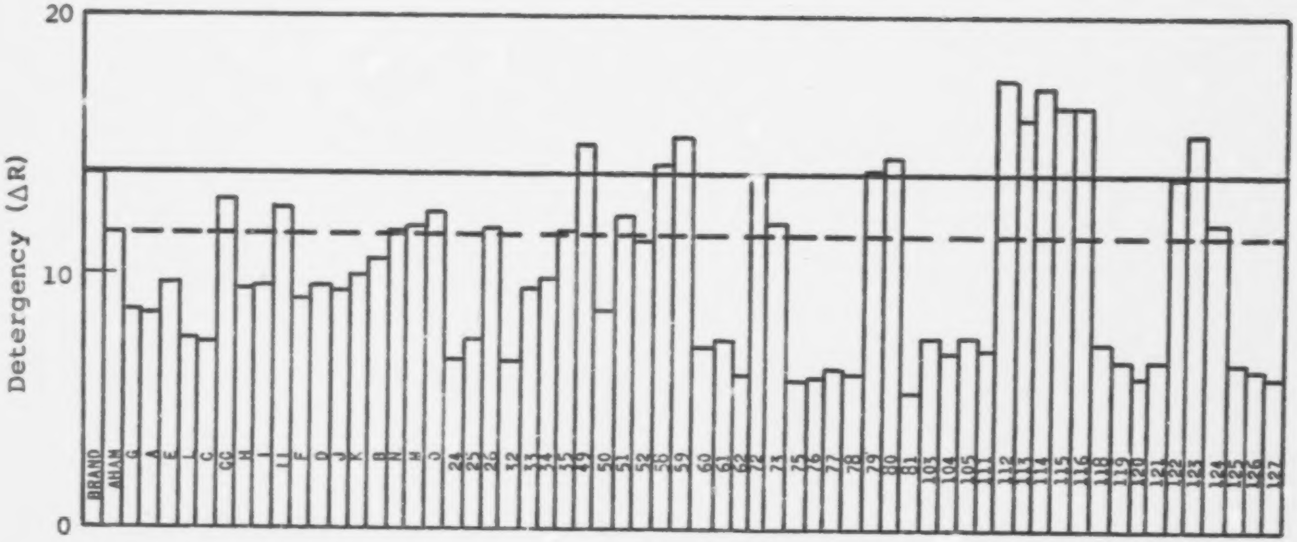


Figure 26

PERFORMANCE OF COMPOUND 112A FORMULATIONS ON UST CLOTH
50 ppm Water Hardness - 0.1% Formulation in Wash Water

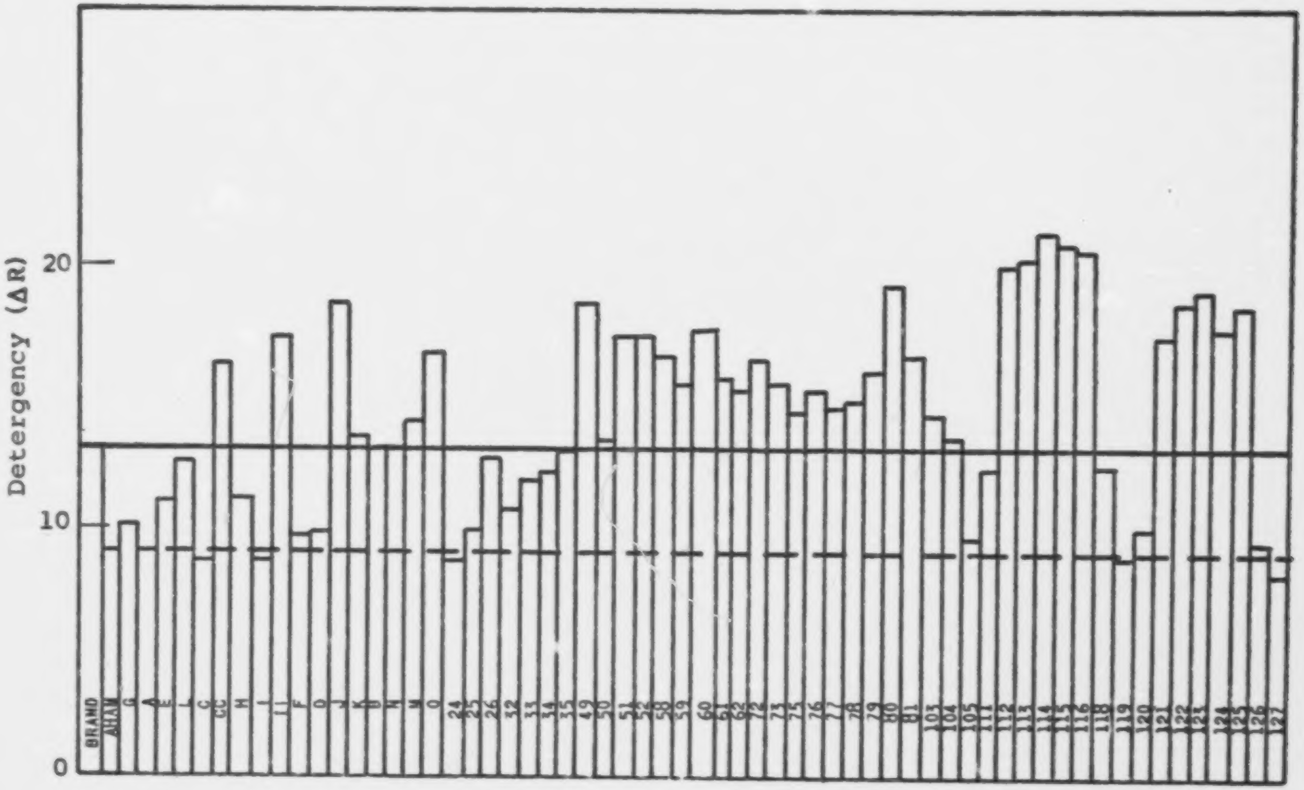


Figure 27

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON UST CLOTH
135 ppm Water Hardness - 0.1%
Formulation in Wash Water

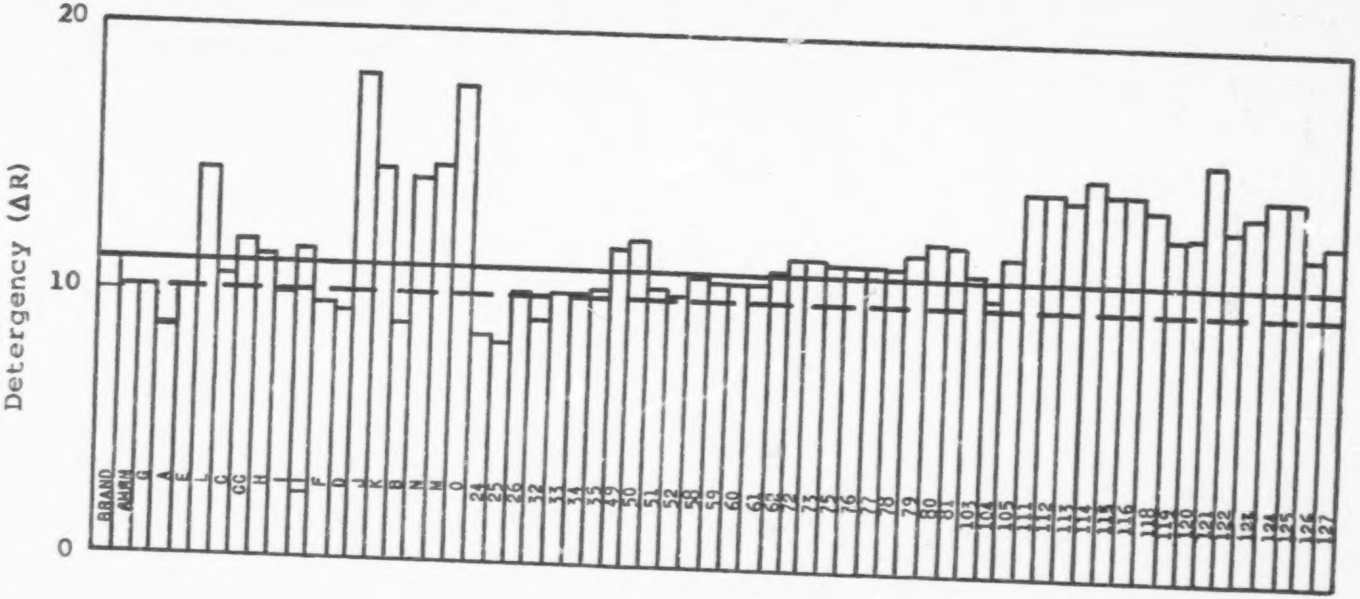


Figure 28

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON UST CLOTH
300 ppm Water Hardness - 0.1%
Formulation in Wash Water

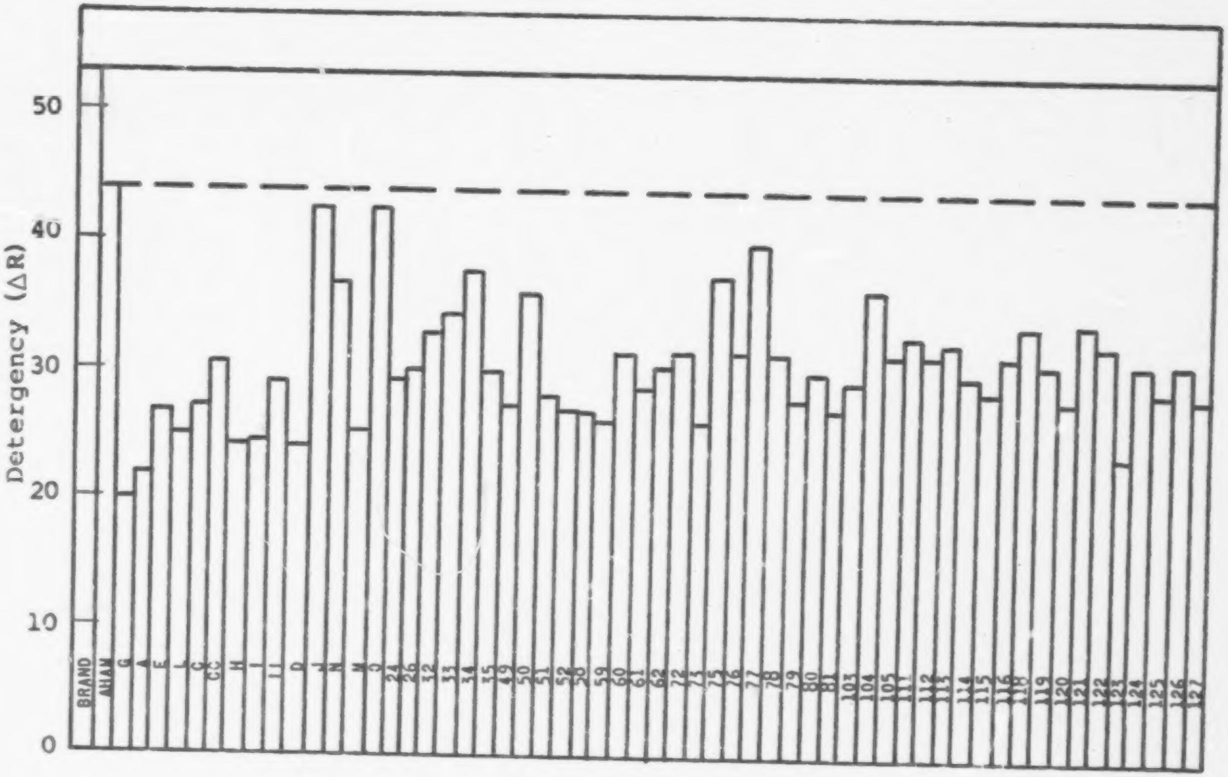


Figure 29

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON EMPA CLOTH
50 ppm Water Hardness - 0.1%
Formulation in Wash Water

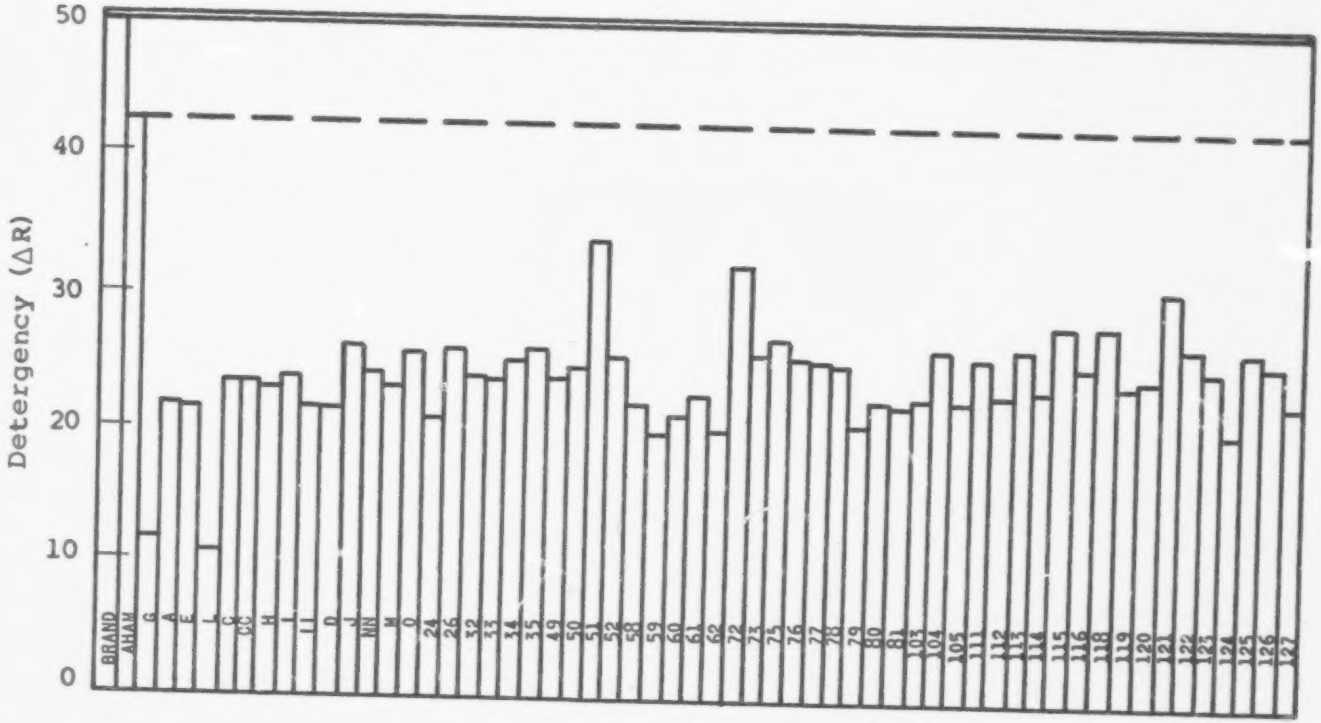


Figure 30

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON EMPA CLOTH
135 ppm Water Hardness - 0.1%
Formulation in Wash Water

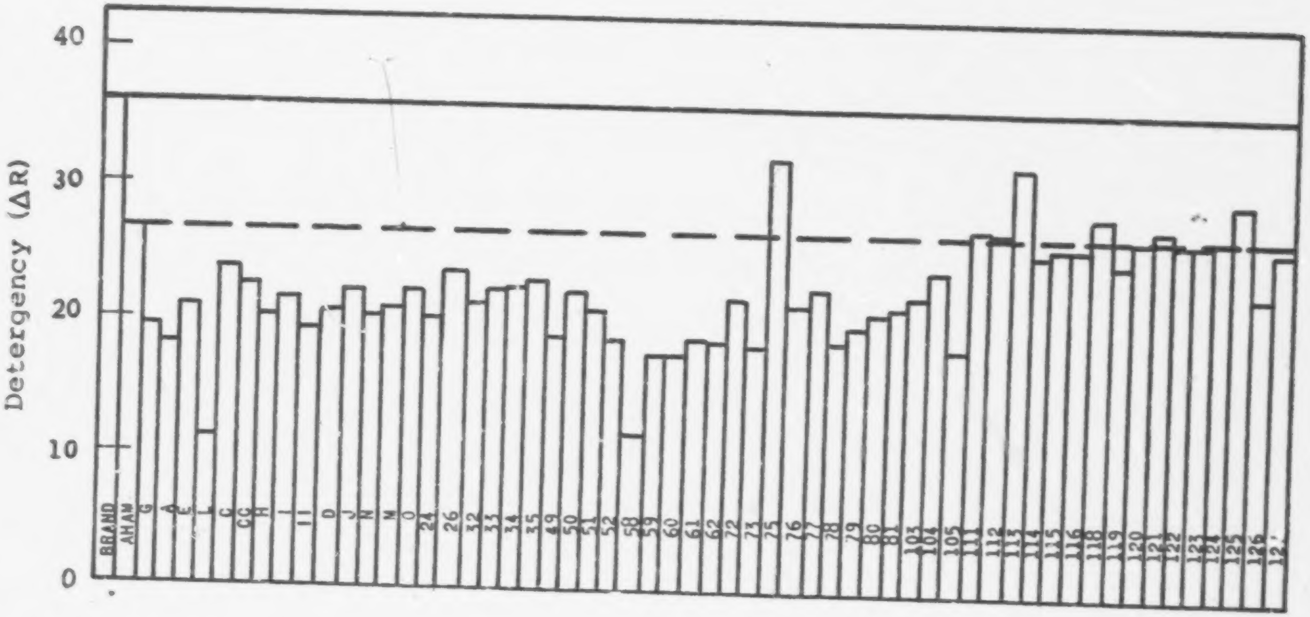


Figure 31

PERFORMANCE OF COMPOUND 112A FORMULATIONS
ON EMPA CLOTH
300 ppm Water Hardness - 0.1%
Formulation in Wash Water

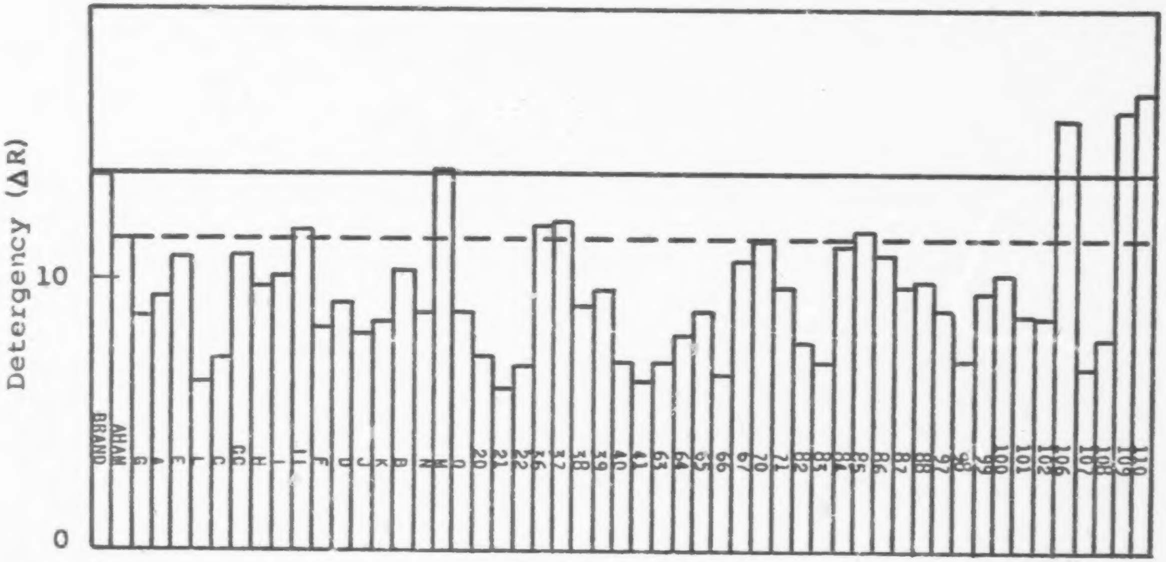


Figure 32

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON UST CLOTH
50 ppm Water Hardness - 0.1%
Formulation in Wash Water

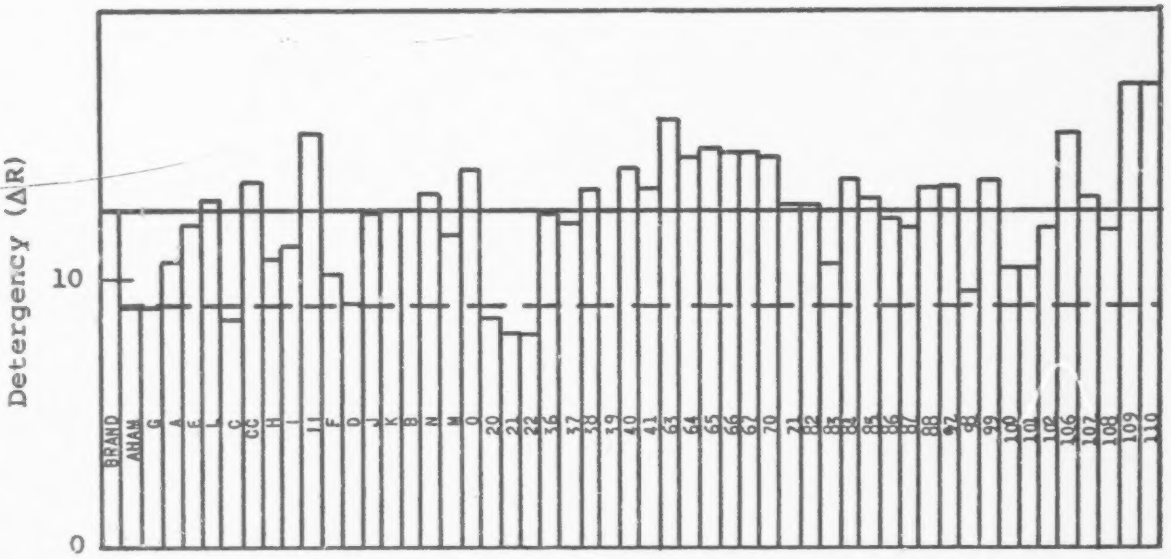


Figure 33

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON UST CLOTH
135 ppm Water Hardness - 0.1%
Formulation in Wash Water

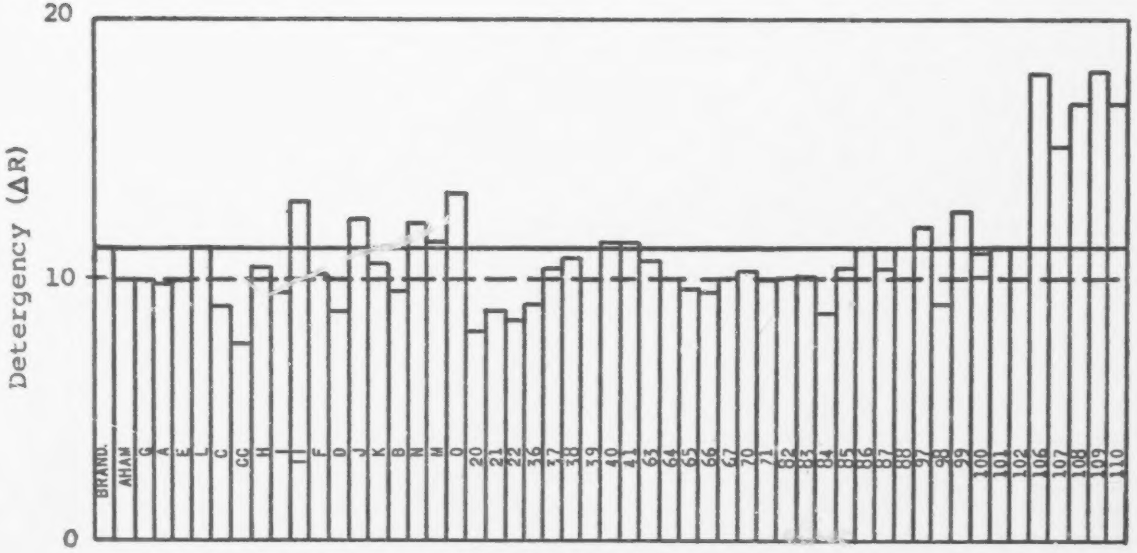


Figure 34

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON UST CLOTH
300 ppm Water Hardness - 0.1%
Formulation in Wash Water

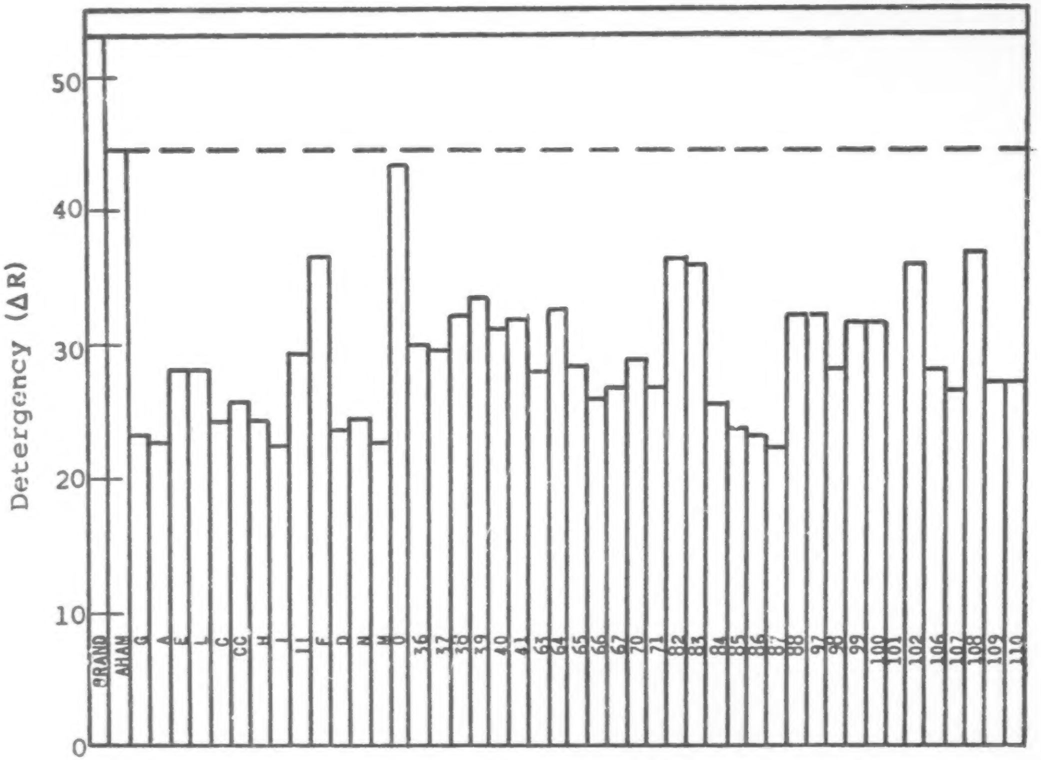


Figure 35

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON EMPA CLOTH
50 ppm Water Hardness - 0.1%
Formulation in Wash Water

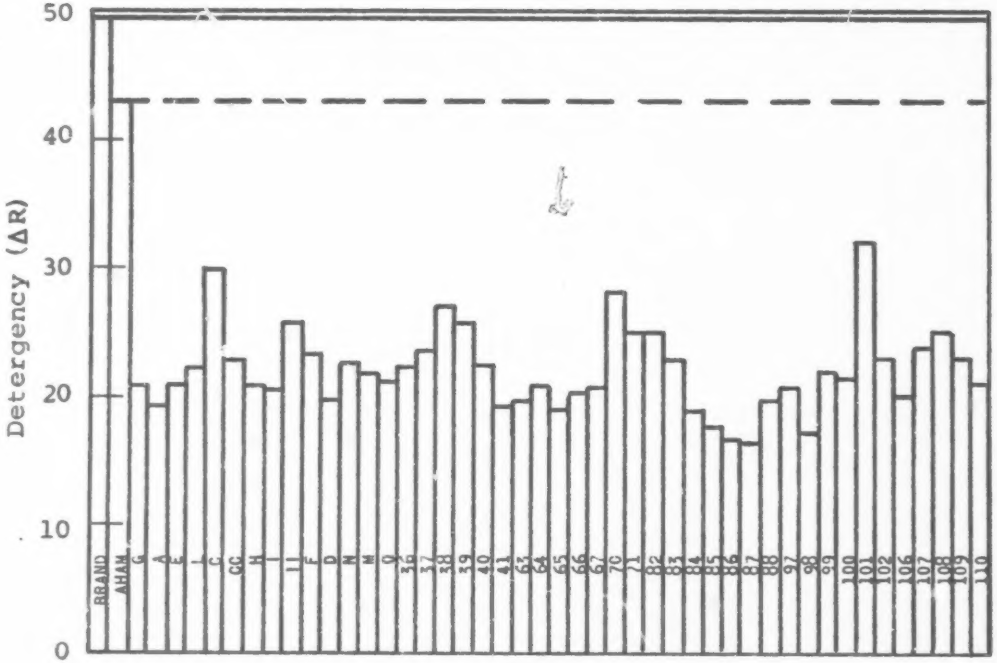


Figure 36

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS ON EMPA CLOTH
135 ppm Water Hardness - 0.1% Formulation in Wash Water

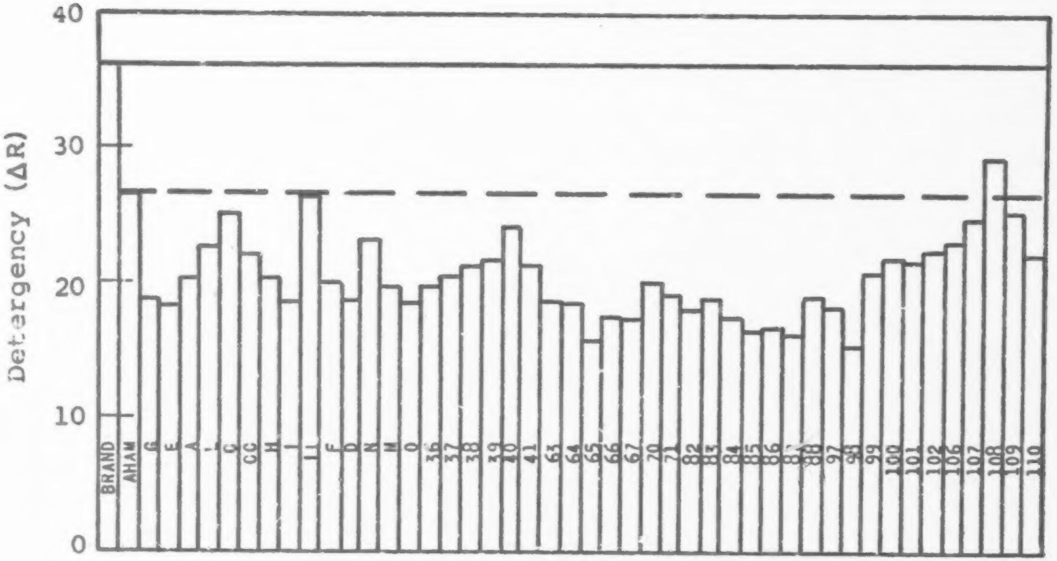


Figure 37

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON EMPA CLOTH
300 ppm Water Hardness - 0.1%
Formulation in Wash Water

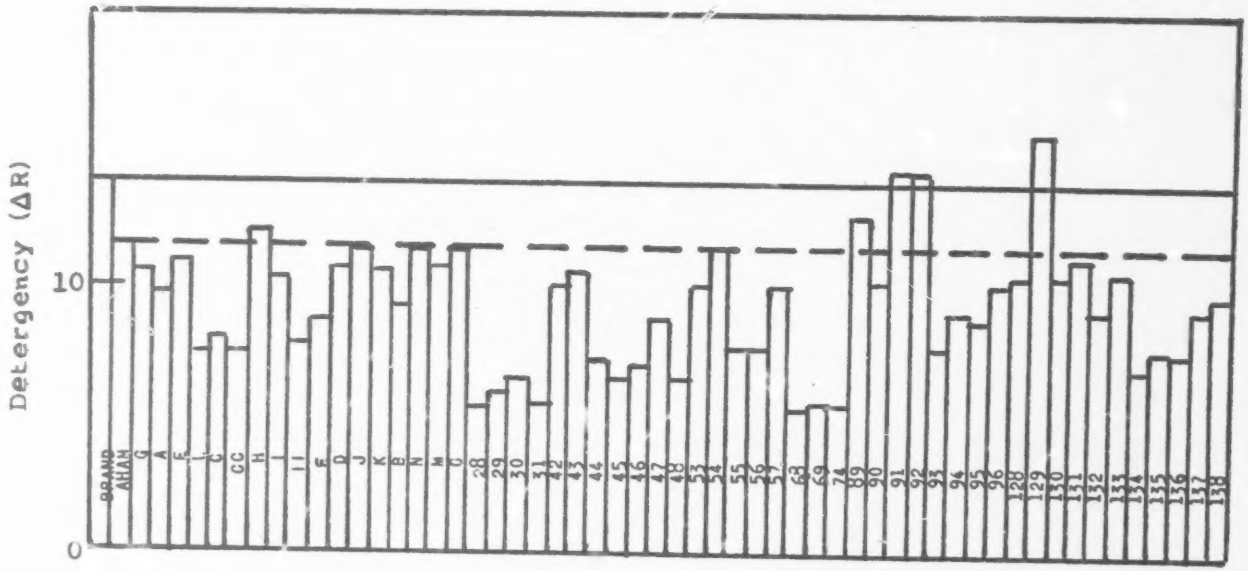


Figure 38

PERFORMANCE OF COMPOUND 112B1 FORMULATIONS
ON UST CLOTH
50 ppm Water Hardness - 0.1%
Formulation in Wash Water

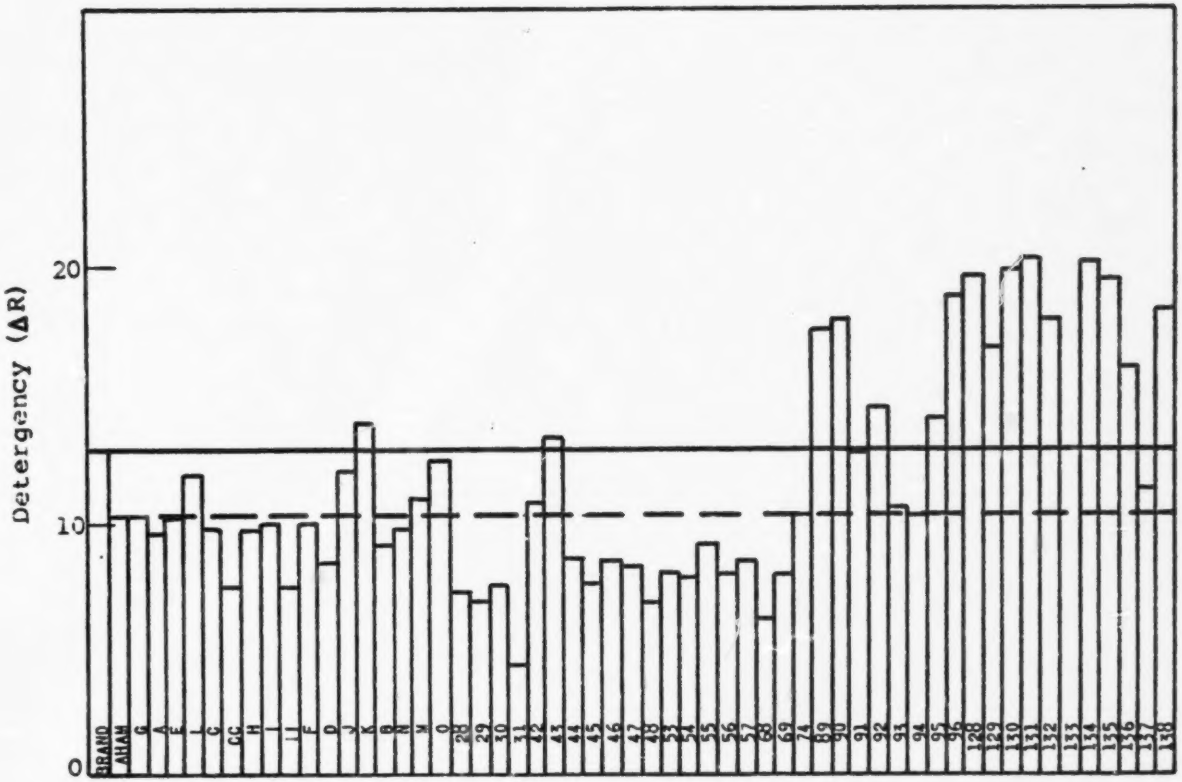


Figure 39

PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON UST CLOTH
135 ppm Water Hardness - 0.1%
Formulation in Wash Water

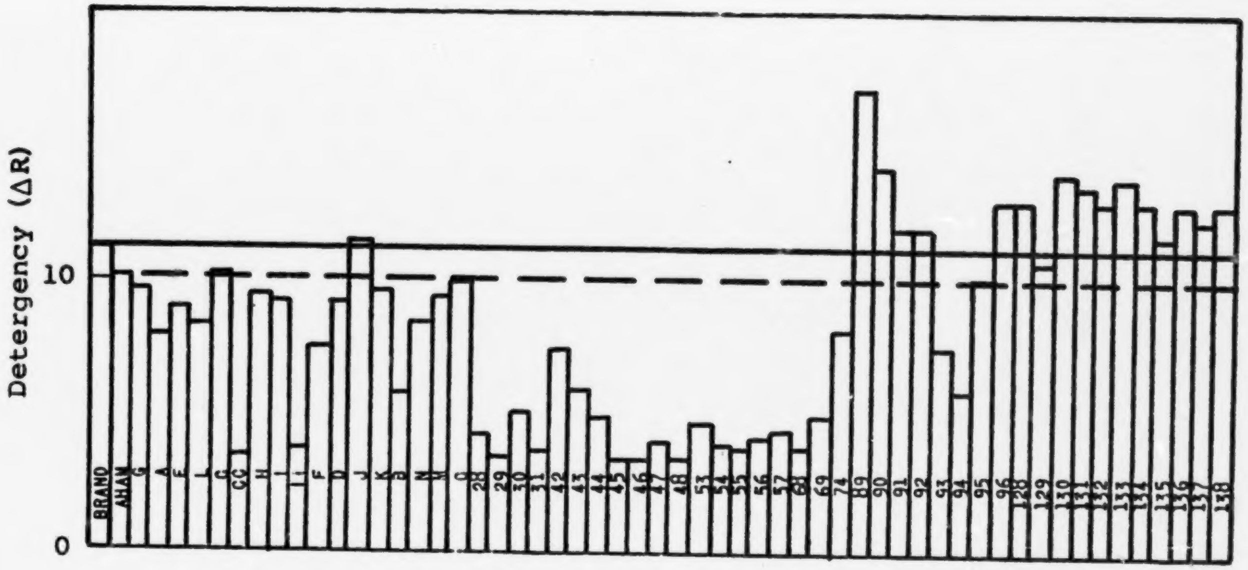


Figure 40
PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON UST CLOTH
300 ppm Water Hardness - 0.1%
Formulation in Wash Water

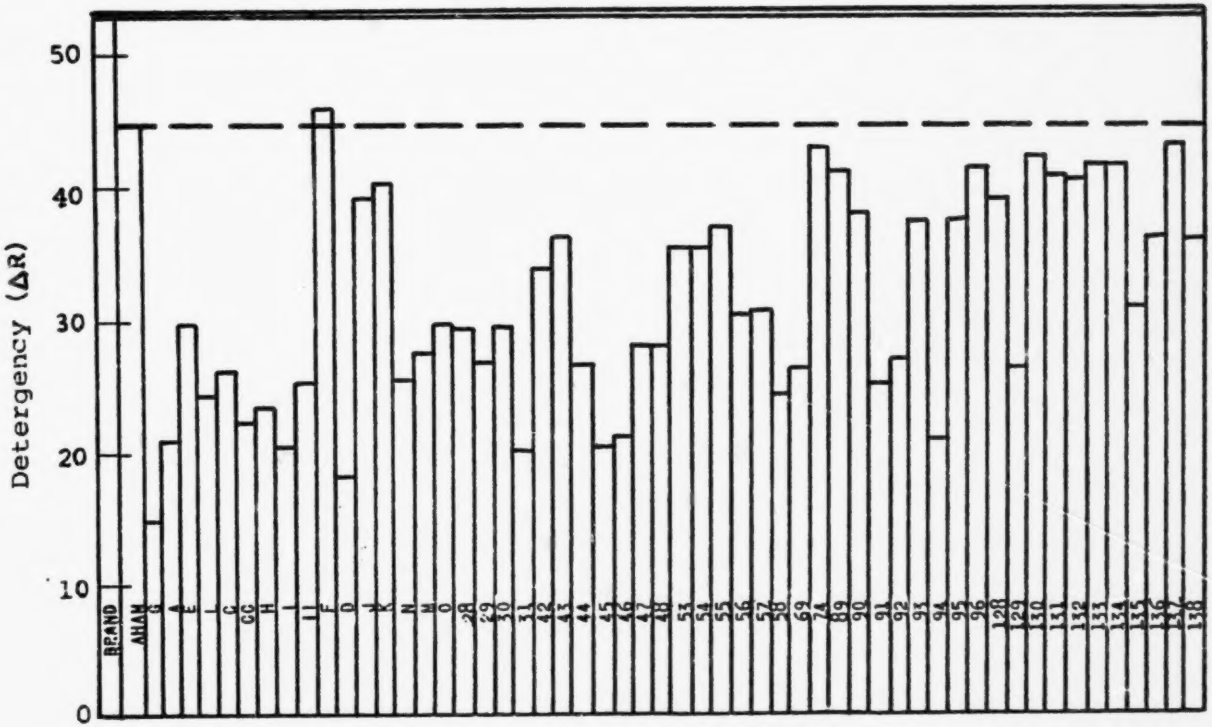


Figure 41

PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON EMPA CLOTH
50 ppm Water Hardness - 0.1%
Formulation in Wash Water

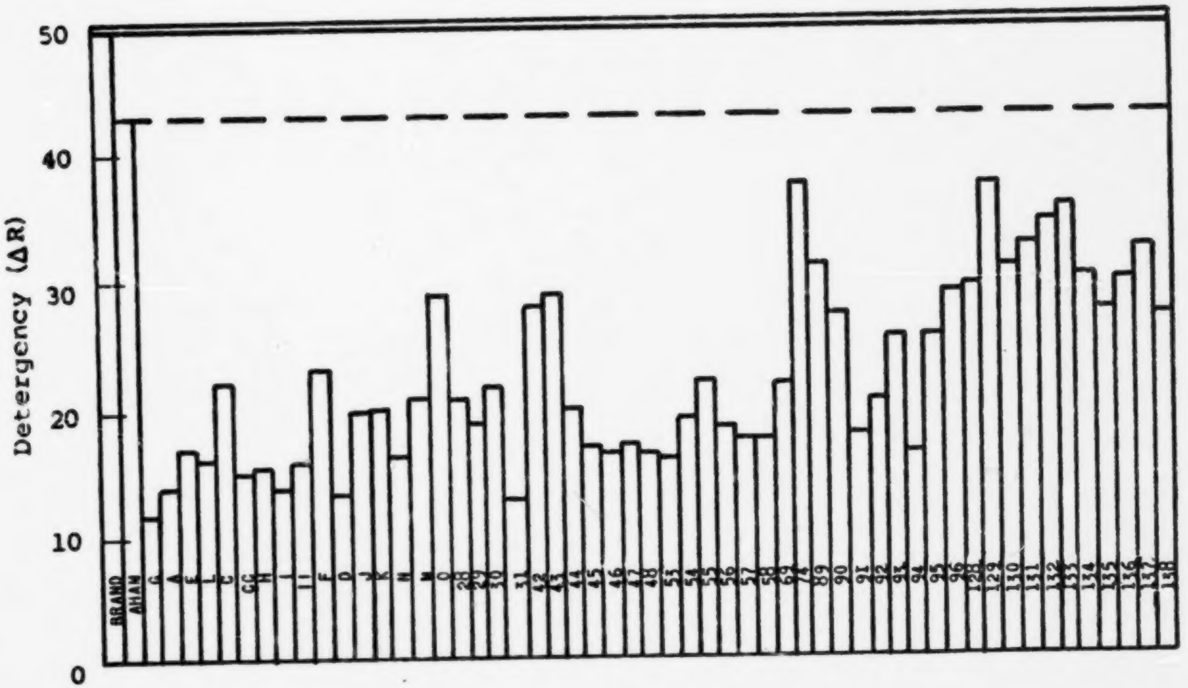


Figure 42

PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON EMPA CLOTH
135 ppm Water Hardness - 0.1%
Formulation in Wash Water

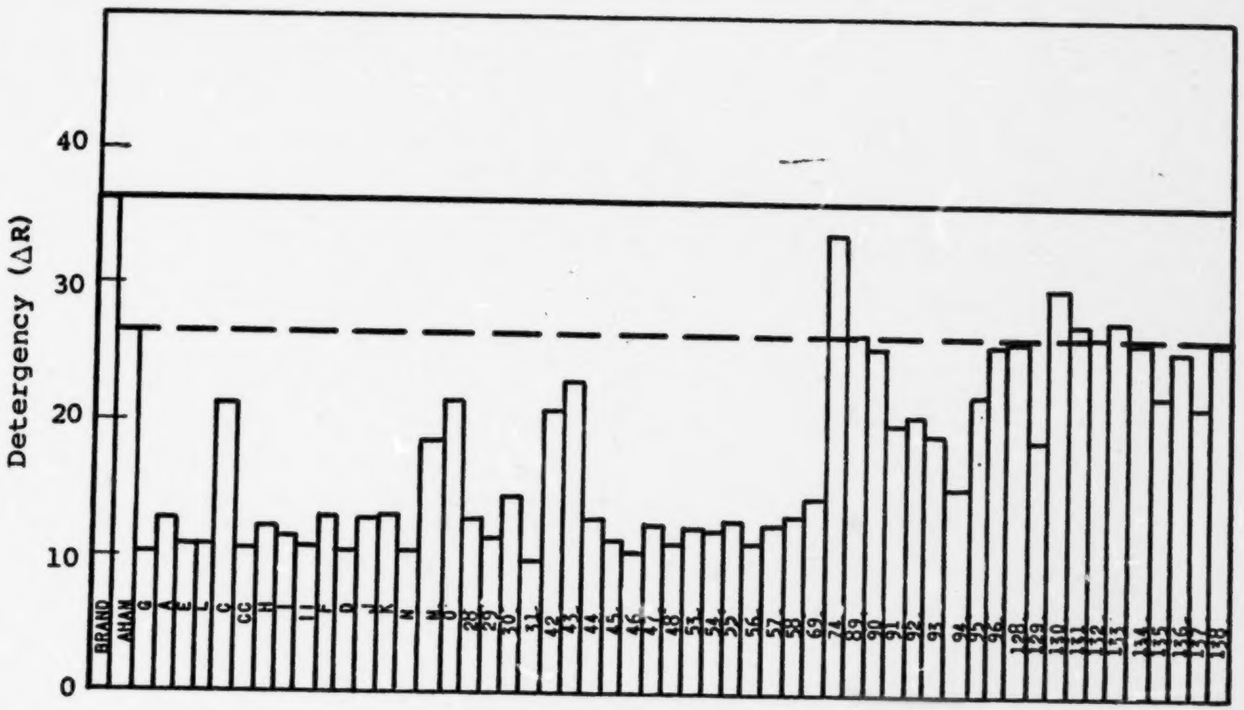


Figure 43

PERFORMANCE OF COMPOUND 212 FORMULATIONS
ON EMPA CLOTH
300 ppm Water Hardness - 0.1%
Formulation in Wash Water

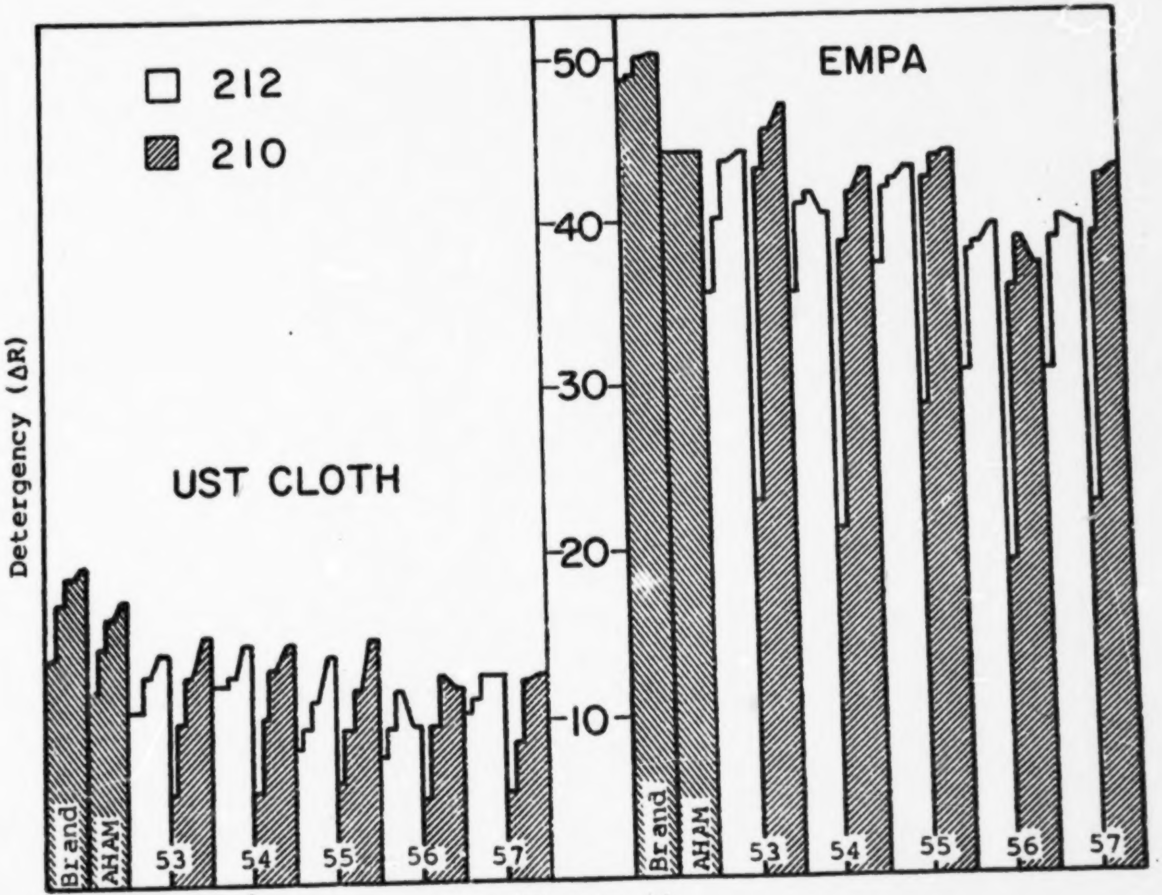


Figure 44

COMPARISON OF COMPOUNDS 212 AND 210
50 ppm Hardness Water

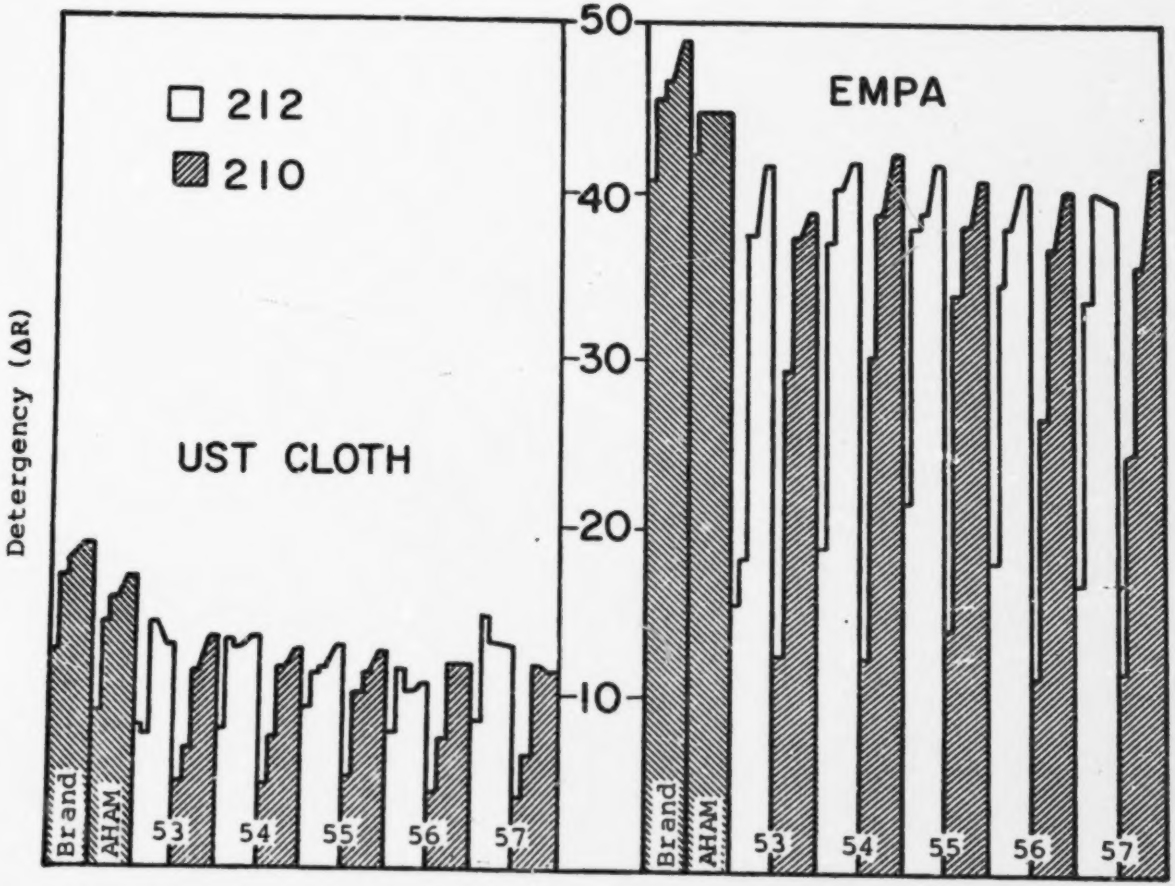


Figure 45

COMPARISON OF COMPOUNDS 212 AND 210
135 ppm Hardness Water

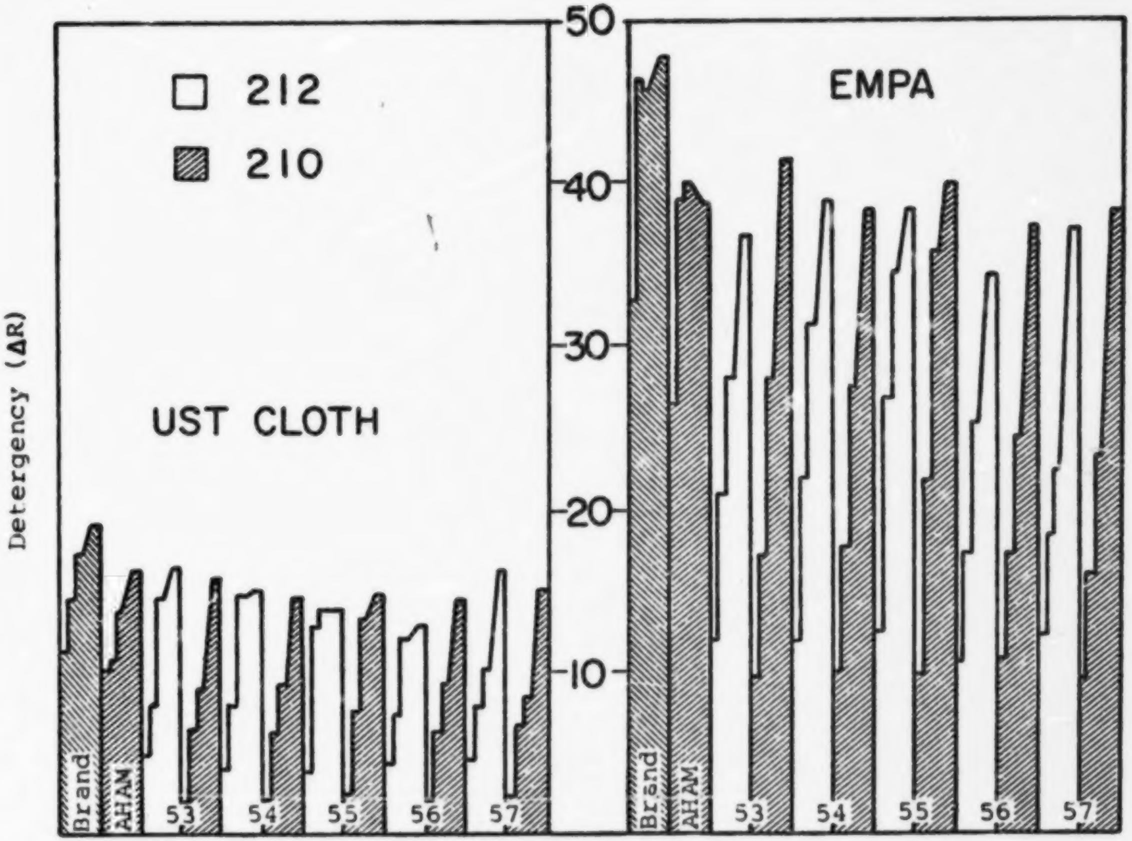


Figure 46

COMPARISON OF COMPOUNDS 212 AND 210
300 ppm Hardness Water

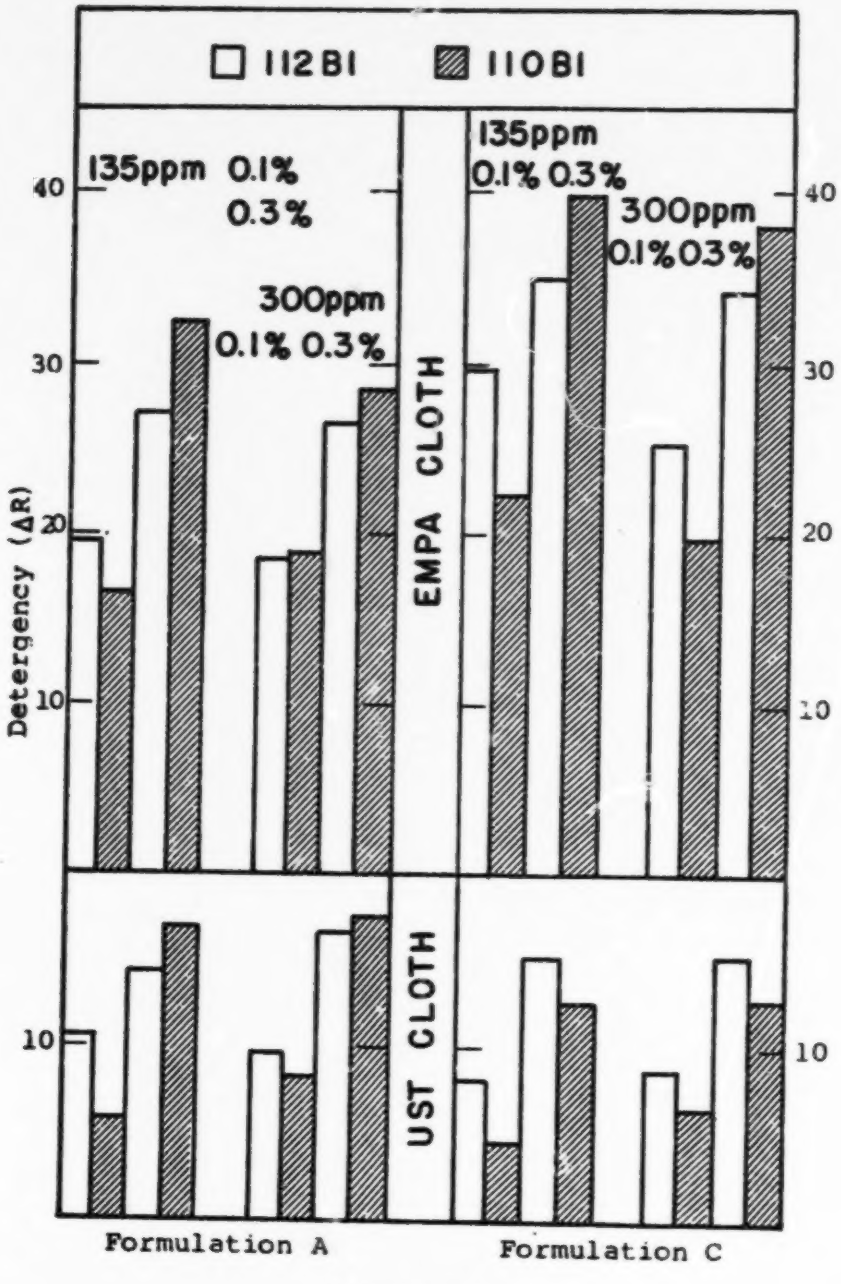


Figure 47
COMPARISON OF 112B1 AND 110B1

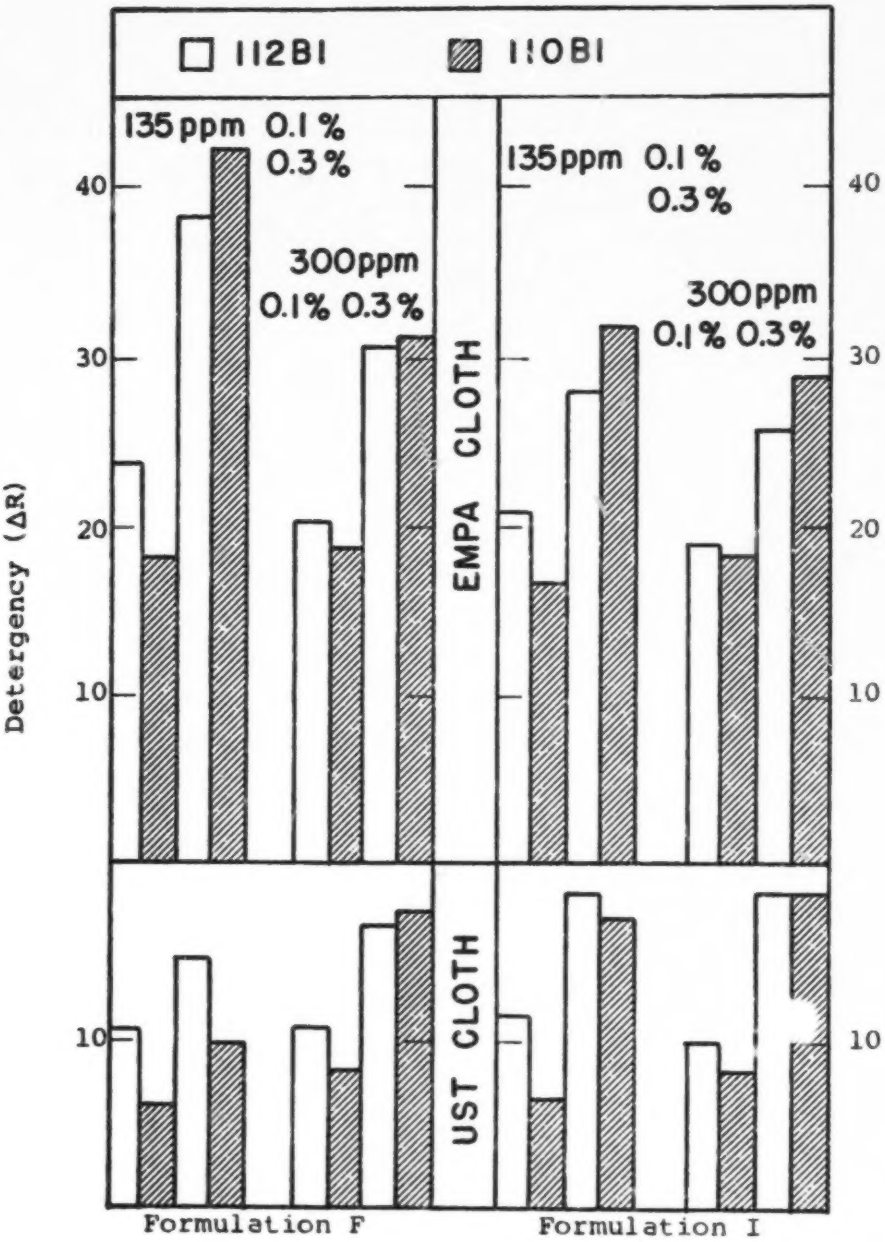


Figure 48

COMPARISON OF 112B1 AND 110B1

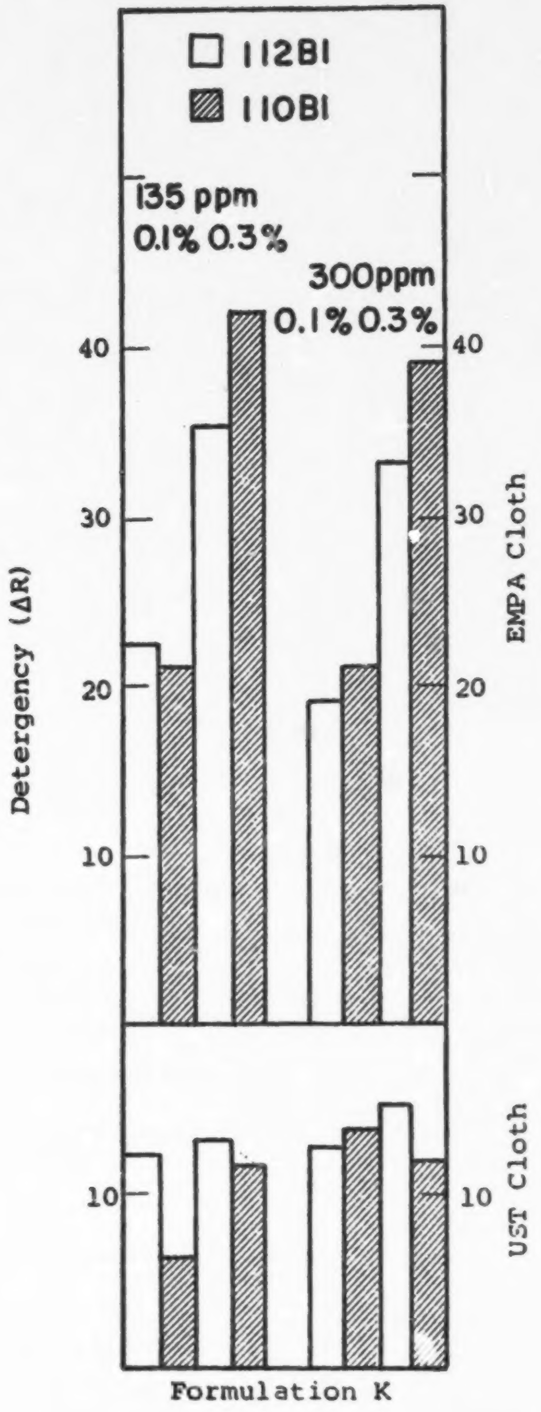


Figure 49

COMPARISON OF 112B1 AND 110B1

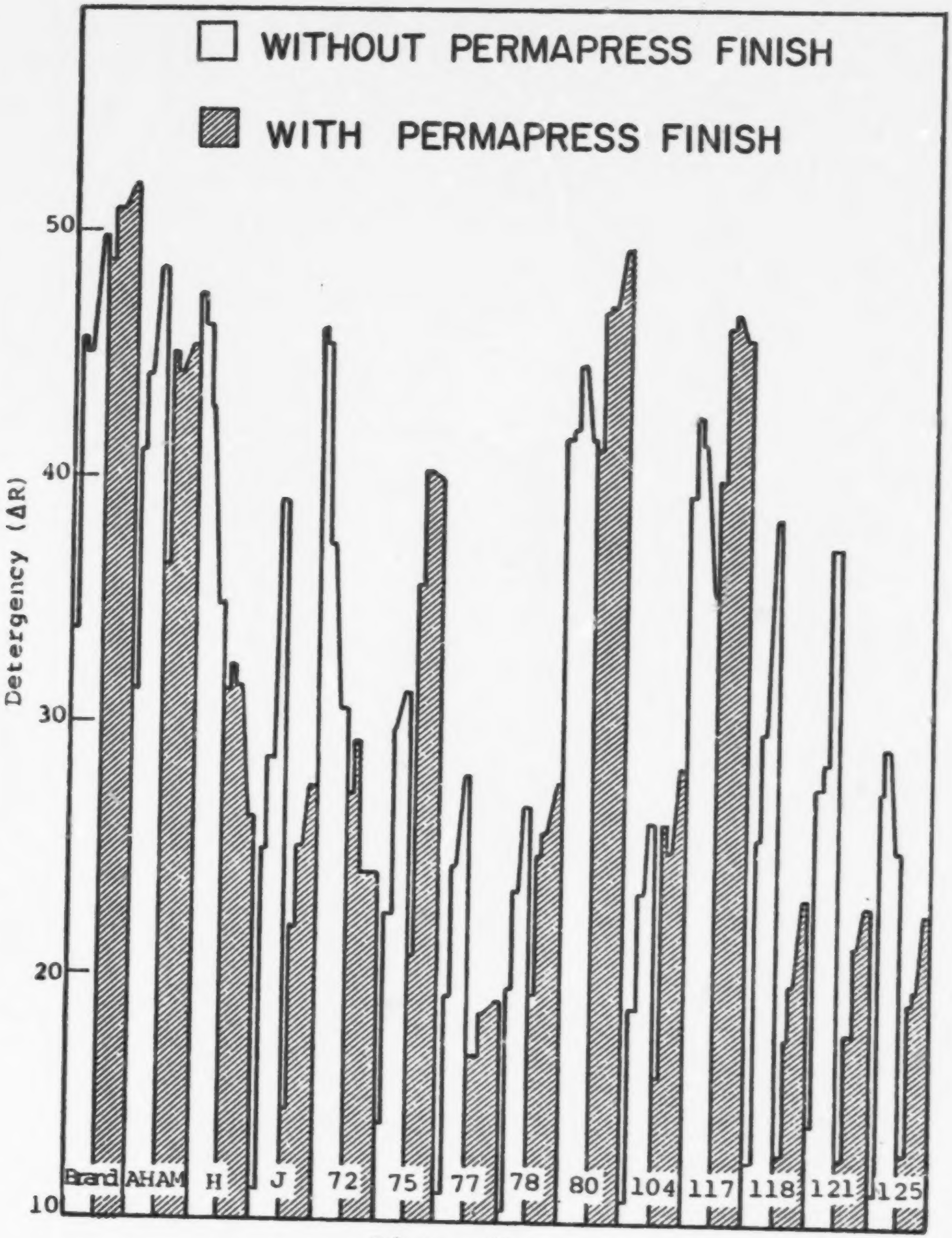


Figure 50

112A FORMULATIONS ON DACRON/COTTON FABRIC
50 ppm Water Hardness

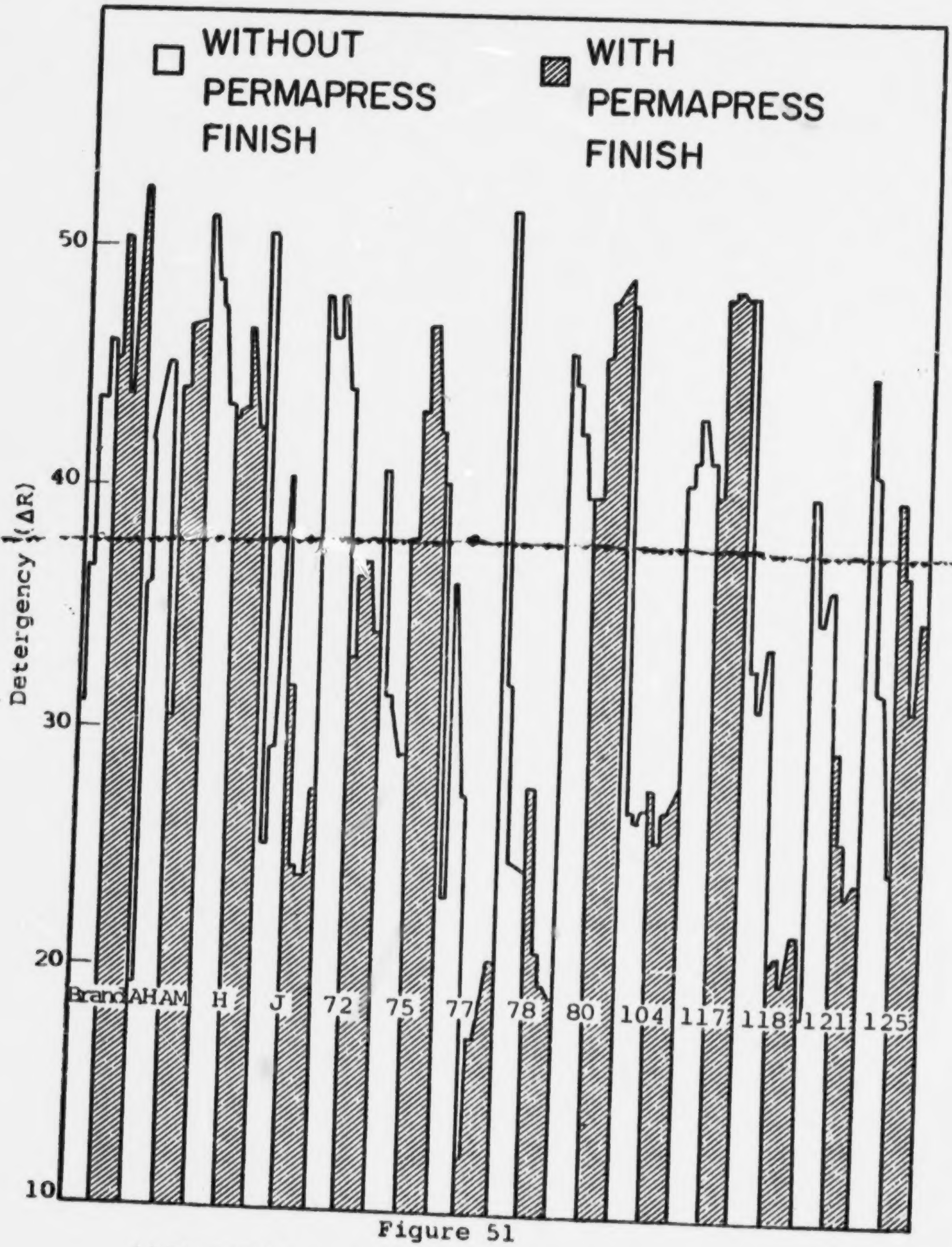


Figure 51
112A FORMULATIONS ON DACRON/COTTON FABRIC
135 ppm Water Hardness

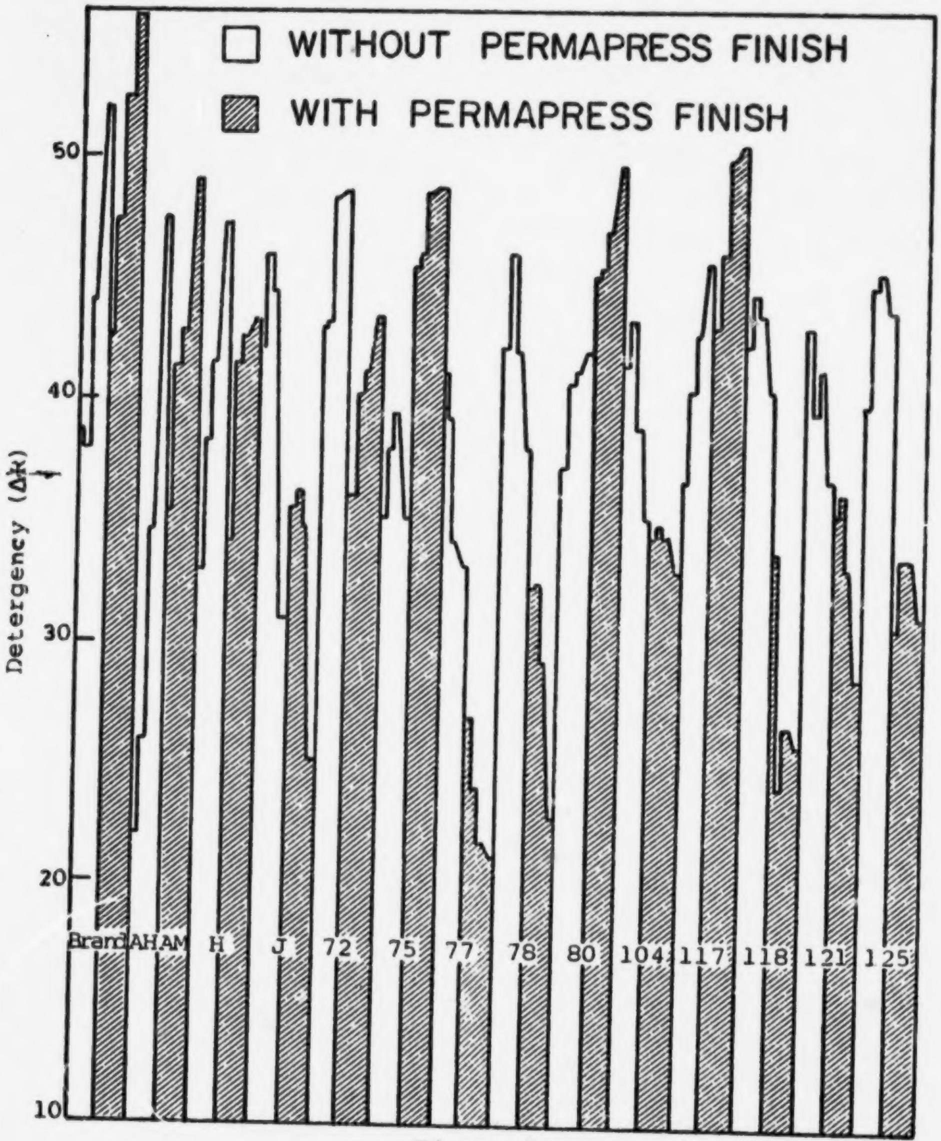


Figure 52

112A FORMULATIONS ON DACRON/COTTON FABRIC
300 ppm Water Hardness

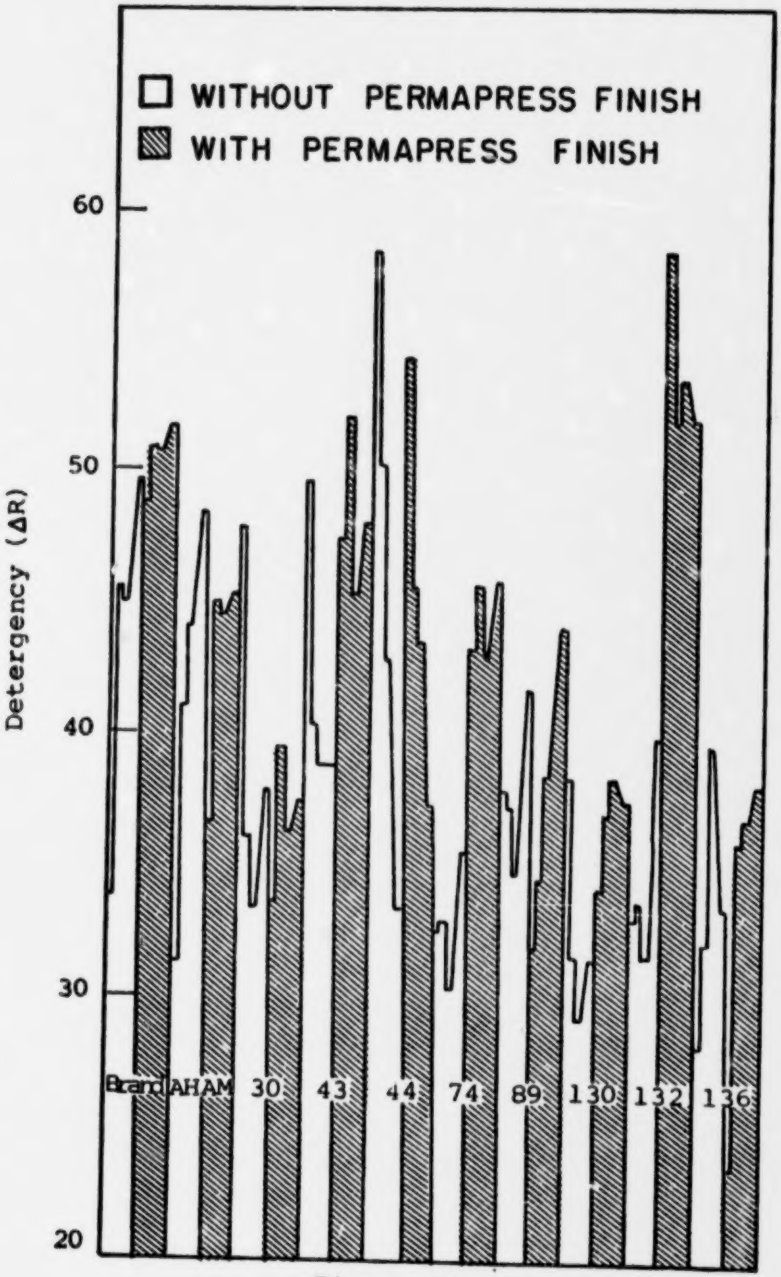


Figure 53

212 FORMULATIONS ON DACRON/COTTON FABRIC
50 ppm Water Hardness

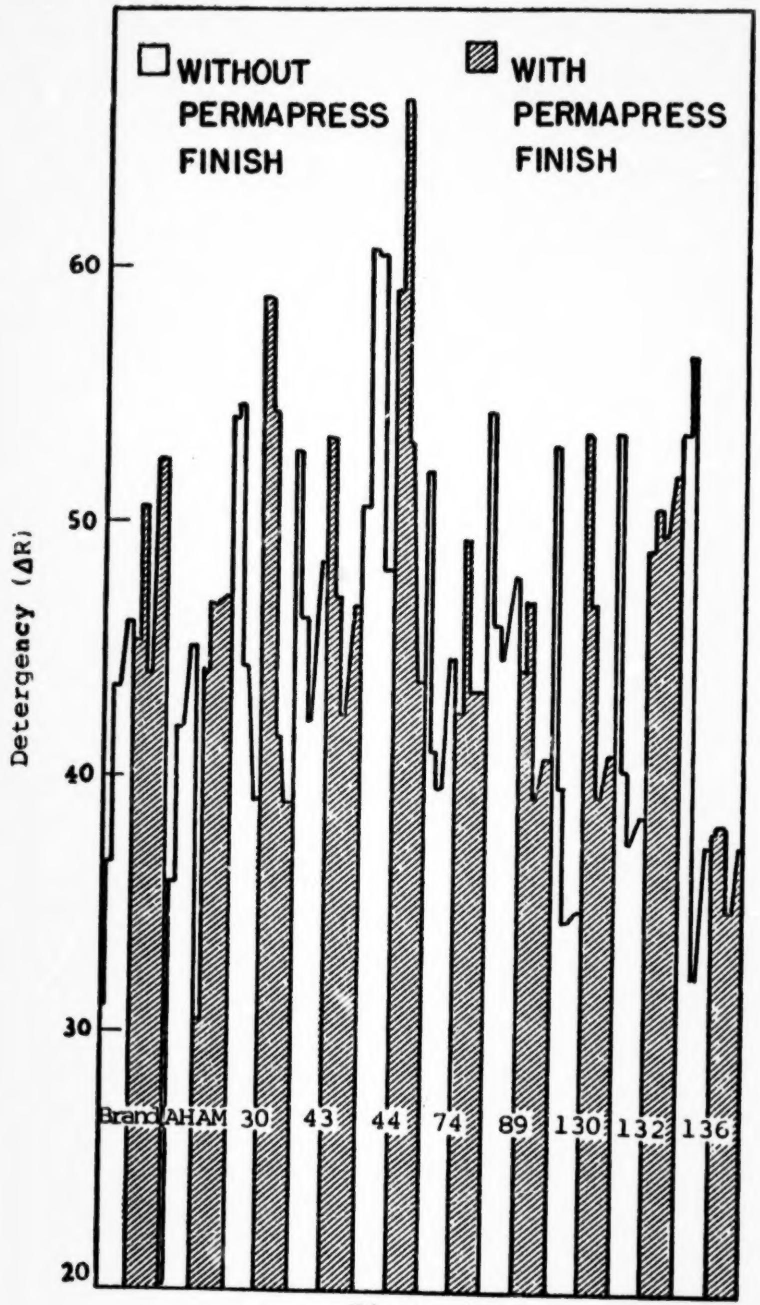


Figure 54

212 FORMULATIONS ON DACRON/COTTON FABRIC
135 ppm Hardness Water

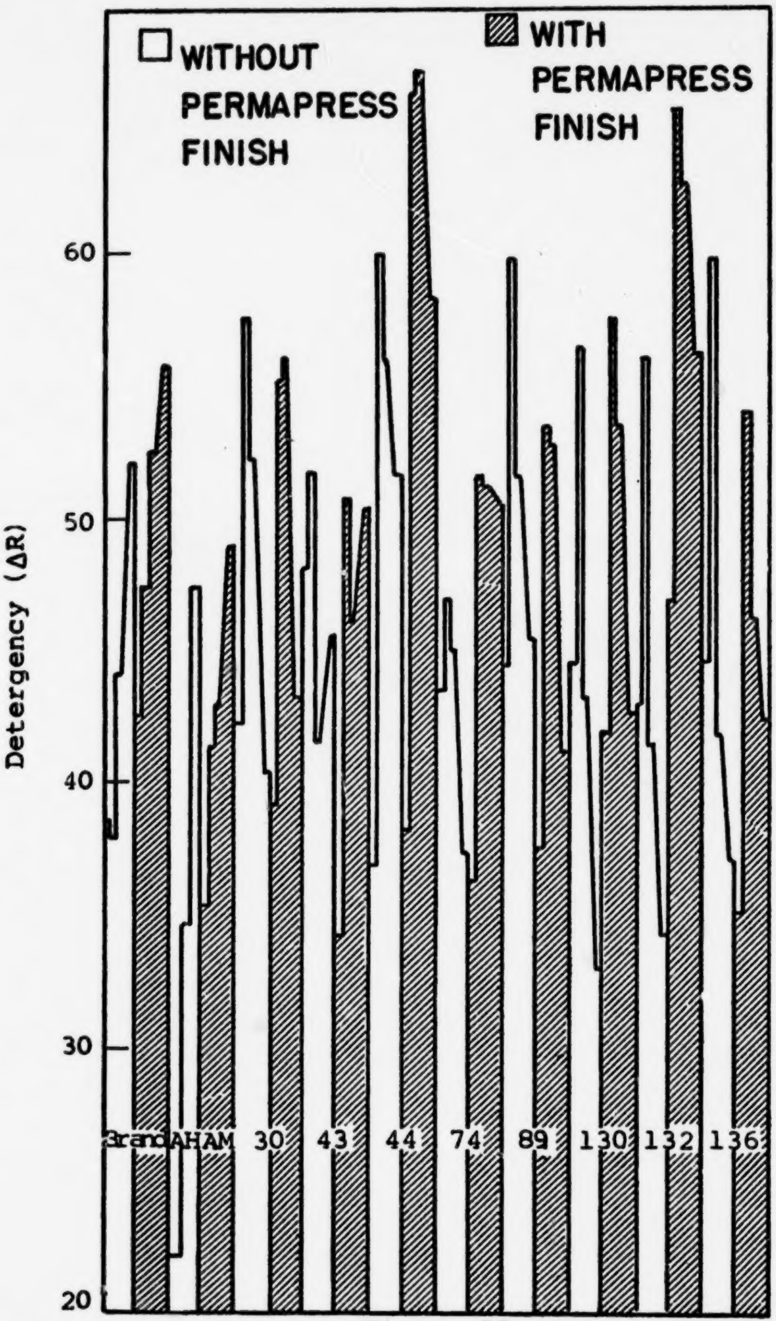


Figure 55

212 FORMULATIONS ON DACRON/COTTON FABRIC
300 ppm Water Hardness

APPENDIX B

Facsimile copy of report from Biometrics.

Biometric

CLIENT: IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616

ATTENTION: Dr. William Linfield

STUDY: TLm 96-hour determination static and dynamic in Fat Head Minnows

TEST MATERIALS:
Compound 112A
Compound 112B1
Compound 212
LAS (control)

EXPERIMENTAL REFERENCE NUMBER: 49-98

DATE: June 8, 1971

Samuel Posner
Director of Environmental Services Division

METHOD

The tolerance limit median (TLm) performed on this study is described by Mount and Brung [1,2] of the Federal Water Pollution Control Administration. Fingerling fathead minnows, 2-4 grams, were acclimated to the laboratory water supply for at least 96 hours prior to range finding test. The fish were fed a standard fish diet and then fasted for 24 hours prior to use. During the test procedure, the animals were fasted so as to minimize the ingestion of test material via the food chain.

The tanks used were 30-gallon all-glass aquaria filled to approximately 16 gallons of pre-filtered water. Water temperature was maintained between 19°C. and 21°C. during the entire test. Dissolved oxygen (O_2) analysis was performed daily during the dynamic phase.

PROCEDURE

Static Phase

Ten to fifteen fingerling fathead minnows per group were exposed to the test compounds in 30-gallon all-glass aquaria. In the static test, the test material was introduced on Day 0, thoroughly mixed and then the fish added. Observations were made at 24-hour and 48-hour intervals. Because this static procedure is for range finding only, it was not necessary to carry the observations beyond 48 hours.

Dynamic Phase

After completing the static range finding phase, two hundred fathead minnows were acclimated as previously described. Six (6) 30-gallon, all-glass tanks, each with 10 fingerlings of approximately 5-8 grams each were used. We were able to maintain a dissolved oxygen (O_2) level of approximately 8-10 ppm. during the course of the dynamic tests. O_2 was maintained daily using the modified Winkler technique[3]. The O_2 value is extremely important so that we can determine the chemical

---

1. Mount, D. I., and Brung, W. A., "A Simplified Dosing Apparatus for Fish Toxicology Studies" Water Res., Vol. I, pp. 21-29, 1967
2. "Water Quality Criteria," FWPCA, April 1968, p. 59
3. Standard Method - Water and Waste Water Analysis, APHA, AWWA, 12th Ed., 1968

oxygen demand (COD) of the test compound and control the O_2 level if necessary by adding pure oxygen. For example, if the COD of the test material is high enough to reduce the O_2 to a level of 4 ppm or less, the fingerlings will die due to the lack of oxygen and not from the direct absorption of the test material.

OBSERVATION

A. Static

Table I summarizes the static TLm 24 hour which were run preparatory to the dynamic phases.

Table I

Compound	TLm 24 hour (ppm)
112A	1.8 - 1.9
112B1	5.5
212	4.0
(1) LAS	6.5
(2) LAS	6.6

The static TLm was read at 24 hours because the rapid degrading (bio-degradation) of the material led us to believe that like active material was left in solution after 24 hours.

(1) original shipment
(2) May 18th shipment

The LAS was run twice using different lots of fish and two different shipments of LAS. (original shipment-2nd shipment May 18th). It should be noted that the TLm 24 hour values are statistically the same.

B. Dynamic

Using the static values the compounds were run on the dynamic system previously described. Table II is a summary of the dynamic data.

Table II

Compound	TLM 96 hour (ppm)	(ppm) Dissolved Oxygen
112A	2.0	8.2-10.4
112B1	6.0	7.8-9.4
212	3.2	7.2-8.0
(1) LAS	12.0	7.2-8.4
(2) LAS	9.5	7.0-8.6

In most cases, other than compound 212, the dynamic TLm is greater than the static value.

DISCUSSION AND CONCLUSION

All the compounds evaluated were readily soluble in water.

The static TLm 24 hour values in most cases were less than the dynamic values. This is most likely due to the biodegradability of the compounds tested.

The water temperature during the dynamic test was maintained between 58-61°F. Dissolved oxygen values for all compounds ranged from approximately 7.0-10.5 ppm.

APPENDIX I

Provisioned Algae Assay Procedures

Test organism: Selenastrum capricornutom

Source: Environmental Protection Agency - FWPCA Laboratory
Corvallis, Oregon

Procedure: PAAP described in Provisional Algae Assay Procedure published in 1969 by the Joint Industry/Government Task Force on Eutrophication

Procedure I, Bottle Test:

METHOD

PAAP procedure, 1969, Bottle Test

A. 125 ml. Erlenmeyer flasks were used as culture vessels.

B. Algae Cell counts were performed by a binocular microscope and a Sedgewick Rafter counting cell.

C. Dry weights were done with an Ainsworth balance by filtering and weighing after oven drying.

PAAP TEST

Compound IIT-112A **Concentrations** 1.4, .14, .014 ppm

DATE: 5/13 - 5/20/71

Compound dilution	Results of Incubation - Cell Counts 5th day No/ml	 Dry Wgt.	 7th day No/ml	 Dry Wgt.
Control	900,000	*	3,000,000	*
Control	416,000		1,083,000	
Control	765,000		3,117,000	
Control	616,000		2,450,000	
Ave.				
1.4ppm	1,233,000		4,717,000	
1.4ppm	2,017,000		5,367,000	
1.4ppm	1,617,000		5,767,000	
1.4ppm	1,533,000		5,633,000	
Ave.				
.14ppm	1,000,000		4,233,000	
.14ppm	1,683,000		4,933,000	
.14ppm	1,617,000		4,850,000	
.14ppm	1,300,000		5,817,000	
Ave.				
.014ppm	1,417,000		3,133,000	
.014ppm	1,000,000		5,083,000	
.014ppm	1,702,000		5,033,000	
.014ppm	1,233,000		3,583,000	
Ave.				

*Table III

PAAP TEST

Compound IIT-212 **Concentrations** 1.8, .18, .018 ppm

DATE:

	Results of Incubation - Cell Counts			
	5th day		7th day	
Compound dilution	No/ml	Dry Wgt.	No/ml	Dry Wgt.
Control	678,000	.00625	3,467,000	*
Control			1,983,000	
Control			2,883,000	
Control			3,350,000	
Ave.				
1.8ppm	911,000	.0125	5,150,000	
1.8ppm			4,317,000	
1.8ppm			4,033.000	
1.8ppm			4,000,000	
Ave.				
.18ppm	589,000	.00632	4,544,000	
.18ppm			3,767,000	
.18ppm			3,567,000	
.18ppm			3,867,000	
Ave.				
.018ppm	589,000	.00632	3,644,000	
.018ppm			6,333,000	
.018ppm			7,615,000	
.018ppm			4,300,000	↓
Ave.				

*See Table III

PAAP TEST

Compound IIT-112B-1 **Concentrations** 3.0, .3, .03 ppm

DATE: 5/4 - 5/11/71

Compound dilution	Results of Incubation - Cell Counts			
	5th day		7th day	
	No/ml	Dry Wgt.	No/ml	Dry Wgt.
Control	127,000	*	1,233,000	*
Control	188,000		2,450,000	
Control	142,000		2,767,000	
Control	293,000		1,017,000	
Ave.				
3.0ppm	170,000		2,283,000	
3.0ppm	203,000		2,933,000	
3.0ppm	288,000		3,850,000	
3.0ppm	417,000		3,450,000	
Ave.				
.3ppm	228,000		2,283,000	
.3ppm	242,000		3,533,000	
.3ppm	313,000		3,483,000	
.3ppm	263,000		4,633,000	
Ave.				
.03ppm	105,000		950,000	
.03ppm	223,000		2,833,000	
.03ppm	78,000		2,150,000	
.03ppm	213,000	↓	1,517,000	↓
Ave.				

*Table III

PAAP TEST

Compound IIT - LAS **Concentrations** 5, .5, .05 ppm

DATE: 4/14 - 4/21/71

Results of Incubation - Cell Counts

Compound dilution	5th day		7th day	
	No/ml	Dry Wgt.	No/ml	Dry Wgt.
Control	1,520,000	*	3,440,000	*
Control	1,550,000		2,230,000	
Control	1,870,000		3,980,000	
Control	1,670,000		2,810,000	
Ave.				
(1) 5.0ppm	116,000		670,000	
5.0ppm	2,110,000		4,570,000	
5.0ppm	2,240,000		5,160,000	
5.0ppm	1,750,000		3,380,000	
Ave.				
.5ppm	1,500,000		7,640,000	
.5ppm	2,180,000		5,110,000	
.5ppm	1,460,000		2,520,000	
.5ppm	1,960,000		3,650,000	
Ave.				
.05ppm	1,060,000		4,520,000	
(1) .05ppm	3,000		6,000	
.05ppm	2,130,000	↓	4,700,000	↓
.05ppm	1,760,000		3,630,000	
Ave.				

*Table III

(1) These two are possibly low because of failure to receive proper inoculation - eliminate from calculations - use 3 replicates.

TABLE III

Equivalent Dry Weight Chart For Selenastrum capricornutom

Concentration of Cells/ml	Equiv. Dry Wgt.
8×10^6	.1 mg/ml
4×10^6	.05
2×10^6	.025
1×10^6	.0125
500,000	.00625

These weights are based upon weights obtained by filtering and weighing after oven drying. These weights should not be considered as accurate as the actual counts made by microscope and a Sedgewick-Rafter counting cell.